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Environmental Considerations of Selected Energy Conserving Manufacturing Process Options: Volume XIV. Primary Copper Industry Report

Arthur D. Little, Inc, Cambridge, Mass.

Prepared for

Industrial Environmental Research Lab, Cincinnati, Ohio.

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ENVIRONMENTAL CONSIDERATIONS OF SELECTED ENERGY CONSERVING MANUFACTURING PROCESS OPTIONS:

Vol. XIV. Primary Copper Industry Report

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16. ABSTRACT

This study assesses the likelihood of new process technology and new practices being introduced by energy intensive industries and explores the environmental impacts of such changes.

Specifically, Vol. XIV deals with the primary copper industry and examines six alternatives: (1) Outokumpu flash smelting, (2) Noranda process, (3) Mitsubishi process, (4) oxygen use in smelting, (5) metal recovery from slags (flotation or electric furnace), and (6) Arbiter process, all in terms of relative economics and environmental/energy consequences. Vol. III-XIII and Vol. XV deal with the following industries: iron and steel, petroleum refining, pulp and paper, olefins, ammonia, aluminum, textiles, cement, glass, chlor-alkali, phosphorus and phosphoric acid, and fertilizers. Vol. I presents the overall summation and identification of research needs and areas of highest overall priority. Vol. II, prepared early in the study, presents and describes the overview of the industries considered and presents the methodology used to select industries.

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ENVIRONMENTAL CONSIDERATIONS OF SELECTED ENERGY CONSERVING MANUFACTURING PROCESS OPTIONS

Volume XIV

PRIMARY COPPER INDUSTRY

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This study, consisting of 15 reports, identifies promising industrial processes and practices in 13 energy-intensive industries which, if implemented over the coming 10 to 15 years, could result in more effective utilization of energy resources. The study was carried out to assess the potential environmental/energy impacts of such changes and the adequacy of existing control technology in order to identify potential conflicts with environmental regulations and to alert the Agency to areas where its activities and policies could influence the future choice of alternatives. The results will be used by the EPA's Office of Research and Development to define those areas where existing pollution control technology suffices, where current and anticipated programs adequately address the areas identified by the contractor, and where selected program reorientation seems necessary. Specific data will also be of considerable value to individual researchers as industry background and in decision-making concerning project selection and direction. The Power Technology and Conservation Branch of the Energy Systems-Environmental Control Division should be contacted for additional information on the program.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

EXECUTIVE SUMMARY

The primary copper industry is one of the most energy intensive industries in the United States, ranking twelfth in terms of energy purchased in the industrial sector. The industry is divided into four segments: mining, beneficiation, smelting, and refining. The U. S. primary refined copper production of over 2 x 10^6 ton/yr is derived from about 25 major mines, 18 smelters, and 16 refineries. About 20% of the refined copper is derived from copper scrap.

All energy forms are used in the copper industry. Melting of the charge materials is accomplished with fossil fuel (natural gas, oil, or pulverized coal firing) or with electric-resistance heating. Electricity is used for electrolysis for recovering and purifying copper by plating it from a solution. Electricity is used for gas, liquid and solid materials handling. Air pollution control has increased gas handling requirements and electricity consumption. The industry traditionally has practiced waste heat recovery from the hot exit gases in order to reduce overall energy requirements.

This report assesses the pollutional consequences of selected new copper process options which may be implemented in the smelting and refining segments of the industry. We have examined six process options in depth. These are Outokumpu flash smelting, the Noranda process, the Mitsubishi process, oxygen use in smelting, metal recovery from slags (flotation or electric furnace), and the Arbiter process. Tables ES-1 and ES-2 summarize our findings with regard to the economic, environmental and energy implications of these six options.

The first three processes (Outokumpu, Noranda, and Mitsubishi) can be considered together. All three are pyrometallurgical processes which use exothermic reactions occurring during smelting to reduce net energy requirements. Use of any one of these new processes could reduce energy consumption by 30-50% (the latter when using oxygen enrichment). The processes are flexible in that they can be fueled by gas, oil, or coal. Compared to the conventional process (which produces a large, dilute, SO_2-containing stream) the new processes produce only concentrated SO_2 streams which can be treated effectively and economically for SO_2 recovery by conversion to sulfuric acid. Therefore, SO_2 emissions are also significantly lower for these processes and a sulfur capture of over 90% is achievable, compared to 50-70% for conventional smelting. At present, it appears that the sulfuric acid can generally be sold only at a price below the full production cost. It is used for leaching, neutralization, or phosphoric acid manufacture. The major hindrance to acceptance of these processes for new installations today is that their applicability to impure concentrates is unproven. Also, because the growth in copper demand is low, few new smelters will be built in the near future. On the other hand, because of EPA regulations on modification of existing smelters, much of the future smelting capacity will result from the construction of new smelters.

TABLE ES-1

QUALITATIVE SUMMARY OF COSTS/ENERGY/ENVIRONMENTAL CONSEQUENCES OF PROCESS OPTIONS IN THE COPPER INDUSTRY

Base Line Process: Conventional Smelting and Refining of Concentrates

PROCESS OPTIONS

	Outokumpu Smelting	Noranda Smelting	Mitsubishi Smelting	Oxygen Use in Smelting	Metal Recovery from Slags		Arbiter Process
					Electric Furnace	Flotation	
COSTS	Slightly higher capital cost. Lower operating cost because of energy savings. Slightly lower air pollution control cost because more concentrated SO_2 streams are handled.	Same as Outokumpu	Same as Outokumpu	Slightly lower capital cost. Slightly higher maintenance requirements. Lower operating costs.	Lower capital cost. Lower operating cost, but lower copper recovery.	Higher capital cost. Higher operating cost, but higher copper recovery.	Lower capital cost at smaller plant size. Higher operating cost.
ENERGY	Lower energy cost use. Overall saving of 30-50%.	Same as Outokumpu	Same as Outokumpu	Lower energy use even after energy used in oxygen manufacture is taken into account.	About the same energy requirements.	About the same energy requirements.	Higher energy requirements. Most of the energy required is in the form of electricity.
ENVIRONMENTAL	Higher levels of sulfur recovery are possible (over 90%). Minimal or no water pollution. Solid waste problem unchanged. No change in feedstock but possible changes in impurity distributions which might require different product treatment.	Same as Outokumpu	Same as Outokumpu	No major change. Possible change in impurity distributions which might require different product treatment.	Solid waste problem unchanged. No water pollution.	Solid waste of finer particle size. Potential water pollution problem.	Minimal air pollution. Change in type of solid wastes generated. Some aqueous effluents.

TABLE ES-2

QUANTITATIVE COMPARISON OF BASE LINE AND ALTERNATIVE PROCESSES IN THE COPPER INDUSTRY

	Reverb Smelting (Base Case)	Electro-Refining (Base Case)	Outokumpu Smelting		Noranda Smelting	Mitsubishi Smelting	Slag Cleaning		Arbiter Process
			No Oxygen	Oxygen			Electric Furnace	Flotation	
• Environmental									
Pollution Control Costs ($/ton of Copper)	54-64	-	59	59	46	59	15	1.90	-
• Energy Consumption									
10^6 Btu/ton of Copper[a]	23-26	4.6	15	13.2	12.5	12	1.2^c	0.8^c	61
• Process Economics									
Investment ($/annual ton)	650-750	450	750	500	750	750	9.5^c	20^c	1000
Pollution Control and Operating Cost ($/ton)[b]	340-370	230	336	259	336	333	$10.47^{c,d}$	$12.40^{c,d}$	636

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[a] Includes electricity at 10,500 Btu/kWh; oxygen at 360 kWh/ton.

[b] Includes pre-tax return on investment - excludes concentrate cost.

[c] $/ton of slag.

[d] Equivalent to about $200-360/ton of recovered copper.

The use of oxygen in smelting decreases fuel requirements and is energy efficient overall since the decrease in fuel requirements is usually larger than the energy required for oxygen separation. Other than higher operating temperatures and the resulting increased maintenance, we can see no real disadvantages to this option.

The two processes for recovering copper from slag remove a major constraint in conventional smelting: the need to maintain a low matte grade in the primary smelting unit to minimize copper losses in the slag. These processes are, therefore, important adjuncts to the new smelting processes which operate at high matte grades as well as being potentially usable in existing smelters. Both flotation and electric furnace can decrease flux requirements in smelting, increase the overall recovery of copper in some cases, and improve smelting unit operations. Operating costs for electric furnace cleaning are lower, but the higher costs of slag flotation are compensated for by higher copper recovery. Energy requirements for both processes are about equal. Both processes produce solid waste. However, that from flotation has a much smaller particle size and requires different disposal/storage techniques.

The Arbiter process (a hydrometallurgical process) is significantly more expensive for treating chalcopyrite concentrates than conventional smelting and refining. The process is less polluting but uses more energy than the conventional technology. The major advantage of the process is its ability to operate on a small scale (30,000-40,000 ton/yr copper) compared to smelting which requires a minimum plant size of over 100,000 ton/yr of copper.

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During the course of the study we also had occasion to contact many individuals within industry and trade associations. Where appropriate we have made reference to these contacts within the various reports. Frequently, however, because of the study's emphasis on future developments with comparative assessments of new technology, information given to us was of a confidential nature or was supplied to us with the understanding that it was not to be credited. Therefore, we extend a general thanks to all those whose comments were valuable to us for their interest in and contribution to this study.

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ENGLISH-METRIC (SI) CONVERSION FACTORS

To Convert From	To	Multiply By
Acre	Metre^2	4,046
Atmosphere (normal)	Pascal	101,325
Barrel (42 gal)	Metre^3	0.1589
British Thermal Unit	Joule	1,055
Centipoise	Pascal-second	0.001
Degree Fahrenheit	Degree Celsius	$t^\circ_c = (t^\circ_F - 32)/1.8$
Degree Rankine	Degree Kelvin	$t^\circ_K = t^\circ_R/1.8$
Foot	Metre	0.3048
Foot^3/minute	Metre^3/sec	0.0004719
Foot^3	Metre^3	0.02831
Foot^2	Metre^2	0.09290
Foot/sec	Metre/sec	0.3048
Foot^2/hr	Metre^2/sec	0.00002580
Gallon (U.S. liquid)	Metre^3	0.003785
Horsepower (550 ft-lbf/sec)	Watt	745.7
Horsepower (electric)	Watt	746.0
Horsepower (metric)	Watt	735.5
Inch	Metre	0.02540
Kilowatt-hour	Joule	3.60×10^6
Litre	Metre^3	1.000×10^{-3}
Micron	Metre	1.000×10^{-6}
Mil	Metre	0.00002540
Mile (U.S. statute)	Metre	1,609
Poise	Pascal-second	0.1000
Pound force (avdp)	Newton	4.448
Pound mass (avdp)	Kilogram	0.4536
Ton (assay)	Kilogram	0.02916
Ton (long)	Kilogram	1,016
Ton (metric)	Kilogram	1,000
Ton (short)	Kilogram	907.1
Tonne	Kilogram	1,000

Source: American National Standards Institute, "Standard Metric Practice Guide," March 15, 1973. (ANS72101-1973) (ASTM Designation E380-72)

I. INTRODUCTION

A. BACKGROUND

Industry in the United States purchases about 27 quads* annually, approximately 40% of total national energy usage.** This energy is used for chemical processing, raising steam, drying, space cooling and heating, process stream heating, and miscellaneous other purposes.

In many industrial sectors energy consumption can be reduced significantly by better "housekeeping" (i.e., shutting off standby furnaces, better thermostat control, elimination of steam and heat leaks, etc.) and greater emphasis on optimization of energy usage. In addition, however, industry can be expected to introduce new industrial practices or processes either to conserve energy or to take advantage of a more readily available or less costly fuel. Such changes in industrial practices may result in changes in air, water or solid waste discharges. The EPA is interested in identifying the pollution loads of such new energy-conserving industrial practices or processes and in determining where additional research, development, or demonstration is needed to characterize and control the effluent streams.

B. CRITERIA FOR INDUSTRY SELECTION

In the first phase of this study we identified industry sectors that have a potential for change, emphasizing those changes which have an environmental/energy impact.

Industries were eliminated from further consideration within this assignment if the only changes that could be envisioned were:

- energy conservation as a result of better policing or "housekeeping,"
- better waste heat utilization,
- fuel switching in steam raising, or
- power generation.

---

*1 quad = 10^{15} Btu

**Purchased electricity valued at an approximate fossil fuel equivalence of 10,500 Btu/kWh

After discussions with the EPA Project Officer and his advisors, industry sectors were selected for further consideration and ranked using:

- Quantitative criteria based on the gross amount of energy (fossil fuel and electric) purchased by industry sector as found in U. S. Census figures and from information provided from industry sources. The primary copper industry purchased 0.081 quads out of the 12.14 quads purchased in 1971 by the 13 industries selected for study, or 0.3% of the 27 quads purchased by all industry (see Table I-1).
- Qualitative criteria relating to probability and potential for process change, and the energy and effluent consequences of such changes.

In order to allow for as broad a coverage of technologies as possible, we then reviewed the ranking, eliminating some industries in which the process changes to be studied were similar to those in another industry planned for study. We believe the final ranking resulting from these considerations identifies those industry sectors which show the greatest possibility of energy conservation via process change. Further details on this selection process can be found in the Industry Priority Report prepared under this contract (Volume II).

On the basis of this ranking method, the primary copper industry appeared in tenth place among the 13 industrial sectors listed.

TABLE I-1

SUMMARY OF 1971 ENERGY PURCHASED IN SELECTED INDUSTRY SECTORS

	Industry Sector	10^{15} Btu's	SIC Code In Which Industry Found
1.	Blast furnaces and steel mills	3.49(1)	3312
2.	Petroleum refining	2.96(2)	2911
3.	Paper and allied products	1.59	26
4.	Olefins	0.984(3)	2818
5.	Ammonia	0.63(4)	287
6.	Aluminum	0.59	3334
7.	Textiles	0.54	22
8.	Cement	0.52	3241
9.	Glass	0.31	3211, 3221, 3229
10.	Alkalies and chlorine	0.24	2812
11.	Phosphorus and phosphoric acid production	0.12(5)	2819
12.	Primary copper	0.081	3331
13.	Fertilizers (excluding ammonia)	0.078	287

(1) Estimate for 1967 reported by FEA Project Independence Blueprint, p. 6-2, USGPO, November 1974.

(2) Includes captive consumption of energy from process byproducts (FEA Project Independence Blueprint)

(3) Olefins only, includes energy of feedstocks: ADL estimates

(4) Ammonia feedstock energy included: ADL estimates

(5) ADL estimates

Source: 1972 Census of Manufactures, FEA Project Independence Blueprint, USGPO, November 1974, and ADL estimates.

C. CRITERIA FOR PROCESS SELECTION

In this study we have focused on identifying changes in the primary production processes which have clearly defined pollution consequences. In selecting those to be included in this study, we have considered the needs and limitations of the EPA as discussed more completely in the Industry Priority Report mentioned above. Specifically, energy conservation has been defined broadly to include, in addition to process changes, conservation of energy or energy form (gas, oil, coal) by a process or feedstock change. Natural gas has been considered as having the highest energy form value followed in descending order by oil, electric power, and coal. Thus, a switch from gas to electric power would be considered energy conservation because electric power could be generated from coal, existing in abundant reserves in the United States in comparison to natural gas. Moreover, pollution control methods resulting in energy conservation have been included within the scope of this study. Finally, emphasis has been placed on process changes with near-term rather than long-term potential within the 15-year span of time of this study.

In addition to excluding from consideration better waste heat utilization, "housekeeping," power generation, and fuel switching, as mentioned above, certain options have been excluded to avoid duplicating work being funded under other contracts and to focus this study more strictly on "process changes." Consequently, the following have also not been considered to be within the scope of work:

- Carbon monoxide boilers (however, unique process vent streams yielding recoverable energy could be mentioned);
- Fuel substitution in fired process heaters;
- Mining and milling, agriculture, and animal husbandry;
- Substitution of scrap (such as iron, aluminum, glass, reclaimed textiles, and paper) for virgin materials;
- Production of synthetic fuels from coal (low-and high-Btu gas, synthetic crude, synthetic fuel oil, etc.); and
- All aspects of industry-related transportation (such as transportation of raw material).

D. SELECTION OF PRIMARY COPPER INDUSTRY PROCESS OPTIONS

Within each industry, the magnitude of energy use was an important criterion in judging where the most significant energy savings might be realized, since reduction in energy use reduces the amount of pollution generated in the energy production step. Guided by this consideration, candidate options for in-depth analysis were identified from the major energy consuming process steps with known or potential environmental problems.

After developing a list of candidate process options, we assessed subjectively

- pollution or environmental consequences of the process change,
- probability or potential for the change, and
- energy conservation consequences of the change.

Even though all of the candidate process options were large energy users, there was wide variation in energy use and estimated pollution loads between options at the top and bottom of the list. A modest process change in a major energy consuming process step could have more dramatic energy consequences than a more technically significant process change in a process step whose energy consumption is rather modest. For the lesser energy-using process steps process options were selected for in-depth analysis only if a high probability for process change and pollution consequences was perceived.

Because of the time and scope limitations for this study, we have not attempted to prepare a comprehensive list of process options or consider all economic, technological, institutional, legal or other factors affecting implementation of these changes. Instead we have relied on our own background experience, industry contacts, and the guidance of the Project Officer and EPA advisors to choose promising process options (with an emphasis on near-term potential) for study in the primary copper industry.

Copper extraction from sulfide ores is traditionally divided into four segments:

- mining - where ore containing 0.6-2% copper is mined;
- beneficiation - where the copper-containing minerals are separated from the waste rock to produce a concentrate containing about 25% copper;
- smelting - where concentrates are melted and reacted to produce 98% pure "blister" copper or "anode" copper (copper 98-99% pure requiring further refining); and
- refining - where blister copper is refined electrolytically to produce 99.9% pure "cathode" copper.

The conventional approach and the potential process changes are shown in Table I-2. Of these, the following candidate process options were considered in order to illustrate as wide a spectrum as possible of the consequences of process change:

- Outokumpu flash smelting,
- Noranda process,
- Mitsubishi process,

TABLE I-2

COPPER EXTRACTION FROM SULFIDES: CONVENTIONAL PROCESSING AND PROCESS OPTIONS

Stage	Process Options	
Mining		
Beneficiation		
Smelting	• Conventional Smelting - Slag Discard* • Outokumpu Smelting* • Noranda Smelting* • Mitsubishi Smelting* • Oxygen Use in Smelting* • Metal Recovery from Slag* • Brixlegg Process • Other Continuous Smelting Processes	• Arbiter Process* • Ferric Ion Leaching of Sulfides • Bacterial Leaching • Sulfuric Acid Leaching of Sulfides Roast-Leach-Electrowin • Nitric Acid Leaching
Refining	• Conventional Electrorefining*	

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*Process options studied in detail in this report.

- Oxygen use in smelting,
- Metal recovery from slags (flotation or electric furnace),
- Arbiter process,
- Sulfuric acid leaching of oxide ores, LIX, electrowinning,
- Ferric ion leaching,
- Brixlegg process,
- Bacterial leaching, and
- Sulfuric acid leaching of sulfides.

From this listing we chose (with the concurrence of the Project Officer) the first six for detailed analyses for the following reasons:

- The first three processes, with a high specific capacity, are representative of the newer pyrometallurgical processes which reduce total energy requirements by 30-50%. From the smelting unit they produce a concentrated stream of sulfur dioxide which can be economically converted to sulfuric acid. The adoption of this technology would avoid the use of reverbs which produce dilute SO_2-containing gas streams. Sulfur capture, 50-70% for current technology, would increase to more than 90%.

- Using oxygen in the smelting process is one way of decreasing fuel and increasing the specific capacity of the newer processes. We believed that an examination of oxygen use might provide an assessment of the fuel savings and the decrease in capital requirements through an increase in specific capacity.

- In conventional smelting, the slag from the smelting furnace is discarded. Since the metal content of the slag increases with matte* grade, the matte grade has to be held low. The ability to economically recover metal from slags makes it possible to use the newer smelting processes mentioned above, all of which operate with much higher matte grades.

- There is considerable interest in the United States in the hydrometallurgical extraction of copper from sulfide concentrates to avoid air pollution problems associated with conventional smelting. We selected the Arbiter process because it is ahead of others in terms of plant construction and plant size and because detailed information about the process has been published.

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*See Glossary

The remaining processes are less important for the following reasons:

- Sulfuric acid leaching of oxides is not a primary copper recovery process but can be considered as an acid neutralization/disposal technique that also recovers copper from resources previously considered as marginal.
- Ferric ion (ferric chloride) leaching and sulfuric acid leaching are processes about which there are not sufficient data for a detailed evaluation.
- Bacterial leaching has long-term potential only in conjunction with solution mining techniques.
- The Brixlegg process has been used only on a small scale. Even fewer data are available on impurity behavior in this process than with the other pyrometallurgical processes, such as Outokumpu, Noranda, and Mitsubishi.

For each process, we evaluated the capital and operating costs to pinpoint economic factors which would influence the adoption of new technology. Operating costs for the base line were also calculated on the same bases. In each case we assumed that the plant would meet existing EPA standards for ambient air quality (SO_2 and particulates) and the 1983 Effluent Limitation Guidelines for aqueous effluents. Our calculations do not include any allowances for future standards affecting trace metals since such standards have not been selected and because there are little or no data on the potential emissions of such trace metals from these processes. In all pyrometallurgical processes, the containment and control of airborne pollutants is a difficult achievement and there will always be certain low levels of uncontrolled fugitive emissions.

There are two issues of controversy in the copper industry, relating primarily to existing smelters. The first is the trade-off between permanent controls and intermittent controls for meeting ambient air quality standards. The technological requirements for meeting ambient air quality standards vary greatly from location to location and there does not appear to be a single technological approach which will be the most cost-effective solution in all cases. The second is the trade-off between single absorption and double absorption acid plants for retrofit applications. Although both these issues will be resolved in the future, they do not affect the evaluation of the process options selected here since we are considering the general application of new technology in new locations where New Stationary Source Standards (double absorption acid plants) apply.

II. FINDINGS, CONCLUSIONS, RECOMMENDATIONS

A. PYROMETALLURGICAL PROCESS

Tables II-1 and II-2 summarize cost/energy/environmental consequences of process options studied in this report.

The new pyrometallurgical processes (Outokumpu, Noranda, and Mitsubishi) have two characteristics which make them more energy efficient and less polluting compared to conventional reverb smelters:

- They utilize the heat of oxidation of sulfur and iron to supply part of the process energy requirements.
- They produce steady concentrated streams of SO_2 suitable for sulfuric acid manufacture.

The reduction in energy consumption is significant, about 30-50% (the latter when coupled with oxygen enrichment). The processes are quite flexible in their ability to use any form of energy: gas, oil, or coal. The reduction in SO_2 emissions is also significant. Compared to sulfur capture of 50-70% for conventional smelting, the new processes achieve a sulfur capture of over 90%. Since only concentrated SO_2 streams are produced, the cost of controlling over 90% SO_2 in the new processes is about the same as that for 50-70% control for conventional smelting.

The forces which would drive the U.S. industry to adopt this technology would be EPA regulations limiting SO_2 emissions, and plant modifications and high energy costs in the future. Other factors should also be considered, however. The U.S. copper industry has traditionally increased capacity by expanding and modifying existing smelters and refineries because of the large capital investment per dollar of revenue potential, relatively low growth in demand, cyclical nature of demand, and the international trade in refined metal. In an inflationary economy the production costs from existing, partially depreciated facilities are much lower than those for new facilities. New Source Performance Standards affecting the copper industry will constrain capacity expansion at existing smelters.

The sulfuric acid produced would have to be utilized or disposed of. The typical western U.S. smelter locations are distant from major sulfuric acid markets, and the sulfuric acid has been utilized for leaching of marginal resources (mine dumps, tailings, oxide ores, etc.) or for making wet process phosphoric acid locally. The leaching of dumps and surface deposits without contamination of groundwater is possible in the arid west but might not be possible in other parts of the United States. As a last resort, neutralization with limestone or the reduction of concentrated SO_2 streams to elemental sulfur would have to be considered. These options would exert their own impacts.

TABLE II-1

QUALITATIVE SUMMARY OF COSTS/ENERGY/ENVIRONMENTAL CONSEQUENCES OF PROCESS OPTIONS IN THE COPPER INDUSTRY

Base Line Process: Conventional Smelting and Refining of Concentrates

	PROCESS OPTIONS						
	Outokumpu Smelting	Noranda Smelting	Mitsubishi Smelting	Oxygen Use in Smelting	Metal Recovery from Slags		Arbiter Process
					Electric Furnace	Flotation	
COSTS	Slightly higher capital cost. Lower operating cost because of energy savings. Slightly lower air pollution control cost because more concentrated SO_2 streams are handled.	Same as Outokumpu	Same as Outokumpu	Slightly lower capital cost. Slightly higher maintenance requirements. Lower operating costs.	Lower capital cost. Lower operating cost, but lower copper recovery.	Higher capital cost. Higher operating cost, but higher copper recovery.	Lower capital cost at smaller plant size. Higher operating cost.
ENERGY	Lower energy cost use. Overall saving of 30-50%.	Same as Outokumpu	Same as Outokumpu	Lower energy use even after energy used in oxygen manufacture is taken into account.	About the same energy requirements.	About the same energy requirements.	Higher energy requirements. Most of the energy required is in the form of electricity.
ENVIRONMENTAL	Higher levels of sulfur recovery are possible (over 90%). Minimal or no water pollution. Solid waste problem unchanged. No change in feedstock but possible changes in impurity distributions which might require different product treatment.	Same as Outokumpu	Same as Outokumpu	No major change. Possible change in impurity distributions which might require different product treatment.	Solid waste problem unchanged. No water pollution.	Solid waste of finer particle size. Potential water pollution problem.	Minimal air pollution. Change in type of solid wastes generated. Some aqueous effluents.

TABLE II-2

QUANTITATIVE COMPARISON OF BASE LINE AND ALTERNATIVE PROCESSES IN THE COPPER INDUSTRY

	Reverb Smelting (Base Case)	Electro-Refining (Base Case)	Outokumpu Smelting		Noranda Smelting	Mitsubishi Smelting	Slag Cleaning		Arbiter Process
			No Oxygen	Oxygen			Electric Furnace	Flotation	
• Environmental									
Pollution Control Costs ($/ton of Copper)	54-64	-	59	59	46	59	15	1.90	-
• Energy Consumption									
10^6 Btu/ton of Copper[a]	23-26	4.6	15	13.2	12.5	12	1.2[c]	0.8[c]	61
• Process Economics									
Investment ($/annual ton)	650-750	450	750	500	750	750	9.5[c]	20[c]	1000
Pollution Control and Operating Cost ($/ton)[b]	340-370	230	336	259	336	333	10.47[c,d]	12.40[c,d]	636

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[a] Includes electricity at 10,500 Btu/kWh; oxygen at 360 kWh/ton.

[b] Includes pre-tax return on investment - excludes concentrate cost.

[c] $/ton of slag.

[d] Equivalent to about $200-360/ton of recovered copper.

Like conventional processes, the newer pyrometallurgical processes offer significant economies of scale, the smallest economic size being approximately 100,000 ton/yr of copper.

The major shortcoming of the new processes is that their applicability to impure concentrates (concentrates high in As, Sb, Bi, Pb, Zn, Se, Te, etc.) is unproven. Until this issue is resolved, the new processes would be utilized for building large smelters to smelt clean concentrates in regions where acid markets are available.

In spite of this, we believe that 3-4 new pyrometallurgical plants (Outokumpu, Noranda, etc.) will be built in the United States by 1985-1990, which would account for about 500,000 ton/yr or about 15% of anticipated production in 1990.

B. OXYGEN USE IN SMELTING

The use of oxygen in smelting decreases fuel requirements and is energy efficient overall because the decrease in fuel requirements is usually larger than the energy required for oxygen separation. The use of oxygen enrichment can increase capacities of existing units and decrease capital costs per unit of output from new units. Lesser benefits are the ability to melt more scrap and the production of more concentrated SO_2 streams in some cases.

We believe that these advantages (and the absence of disadvantages other than higher operating temperatures and consequently increased maintenance) will lead to the widespread adoption of oxygen enrichment.

C. RECOVERY OF METALS FROM SLAG

The new pyrometallurgical processes are economically viable only if the metal contained in the slag from the primary smelting unit can be recovered. Thus, these processes are important adjuncts to the new smelting processes and, in addition, might be used in existing smelters (e.g., treatment of converter slags via flotation). The processes can decrease flux requirements, increase the overall recovery of copper in some cases, and improve smelting unit operations.

Of the two processes, electric furnace cleaning is somewhat cheaper, but the higher copper recovery in slag flotation compensates for the higher costs. The energy requirements are about equal for both processes.

While slag flotation produces a finely ground slag that is different from the slag from conventional processing, this slag can be placed into land disposal areas which have been especially prepared to mitigate the possibility of long-term emissions to the environment. Although the particular handling method will be unique to the geological aspects of the area, it is not expected that slag disposal will present a significant environmental problem.

D. THE ARBITER PROCESS

The Arbiter process is significantly more expensive for treating chalcopyrite concentrates than conventional smelting and refining. We believe that this process will be used on other concentrates with favorable mineralogy, e.g., chalcocite concentrates, in locations distant from sulfuric acid markets and where a full-sized pyrometallurgical plant is risky because of growth in copper demand.

The Arbiter process and hydrometallurgical processes in general are not energy efficient and utilize the same or slightly more energy than conventional smelting and refining. The leached solid wastes will require land disposal into areas prepared to prevent groundwater leaching of soluble substances and to prevent airborne particulates. Because the plant will be located generally in the semi-arid western United States, such a disposal area can be established with a high degree of confidence that long-term, adverse environmental impact will not occur.

E. RESEARCH AREAS

Research in the following areas would provide more information about these processes and might resolve the problems preventing the adoption of these technologies.

1. Impurity Distributions

- The behavior of impurities in each process, their distribution between gas, slag, matte and metallic phases, and forms in which impurities leave the process units (as particulates, slag, etc.).
- In oxygen-enriched smelting, an examination and definition of the changes in impurity distributions resulting from higher temperatures.
- Impurity distributions in hydrometallurgy.
- Impurity forms in waste streams from pyrometallurgical and hydrometallurgical processes.

Reasons: An understanding of impurity distributions is necessary to determine emissions of trace metals and the need for pollution control or process change to prevent these emissions.

2. Impurity Removal

- Methods for removing impurities (e.g., Bi) from blister copper via modified fire-refining procedures. If impurities can be removed from copper, one-step smelting can be used. This would significantly decrease fugitive SO_2 emissions from smelters.
- Methods for removal of arsenic from elemental sulfur produced by SO_2 reduction.
- Techniques for impurity removal from concentrates via pretreatment.

3. **Feedstocks**

- Verifying the applicability of new smelting technology to impure concentrates.
- Verifying the applicability of new smelting technology to smelt calcines from roasters.

4. **Metal Recovery/Separation**

- Methods for separation and recovery of metals from flue dust; in particular, the treatment of flue dust containing arsenic, antimony, lead, and bismuth.
- Methods for the recovery of precious and trace metals from hydrometallurgical residues.
- Methods for the recovery of copper (also zinc and lead) from slag flotation tailings.
- Methods for reduction of copper in slag during pyrometallurgical slag cleaning, e.g., carbon reduction in a rotary converter.
- Conversion of ferric oxide sludge from hydrometallurgical processes to a form suitable for use in other industries.

5. **Miscellaneous**

- High-temperature refractories for oxygen smelting.
- Better process control techniques to reduce manpower requirements, particularly in pyrometallurgy.

III. INDUSTRY OVERVIEW

The United States has ranked first or second among world producers of refined copper since before the turn of the century as shown in Table III-1. Most of the copper mined in the United States is produced in five western states -- Arizona, Utah, New Mexico, Montana and Nevada (Table III-2). In the United States, 27 major mines account for over 95% of the copper output. A major portion of the mine production is accounted for by producers such as Kennecott, Phelps Dodge, Anaconda, Newmont and Inspiration, who are integrated from mining through fabrication. Numerous small companies participate only in mining and beneficiation and sell or arrange for toll treatment of their concentrates at the custom smelters of Asarco. Two of the larger mining companies are Duval and Cyprus.

TABLE III-1

LEADING WORLD PRODUCERS OF REFINED COPPER
(Short Tons)

Rank	Country	1970	1974
1	United States	2,242,700	2,136,600
2	U.S.S.R.[1]	1,185,000	1,433,000
3	Japan	777,500	1,101,200
4	Zambia	640,100	746,000
5	Canada	543,000	616,300
6	Chile	512,700	578,700

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[1] Estimate

Source: "Non-Ferrous Metal Data 1974", American Bureau of Metal Statistics, N.Y.

TABLE III-2

U.S. MINE PRODUCTION OF COPPER
(Short Tons)

State	1968	1970	1972	1974
Arizona	631,300	917,918	908,612	852,650
Utah	228,300	295,738	259,507	230,088
New Mexico	92,300	166,278	168,034	197,374
Montana	64,862	120,412	123,110	133,675
Nevada	72,870	106,688	101,119	83,725
Michigan	74,590	67,543	67,260	67,297
Other[1]	34,708	45,080	37,198	28,781
TOTAL	1,199,290	1,719,657	1,664,840	1,593,590

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[1] California, Colorado, Idaho, Maine, Missouri, Pennsylvania, Tennessee, Oklahoma

Source: U.S. Bureau of Mines, Mineral Yearbook

Copper extraction is traditionally divided into four segments: mining, beneficiation, smelting, and refining. A generalized flowsheet of copper processing is shown in Figure III-1. This report addresses technological changes in smelting and refining.

Smelting practice in the United States is fairly uniform from smelter to smelter. About half of the copper smelters roast their charge prior to feeding to the reverberatory (reverb) furnace (calcine smelting), while the other half feed the concentrates directly (green feed smelting). The subsequent steps consist of melting the charge in the reverberatory furnace to form matte, a mixture of copper and iron sulfides and a slag (which is discarded); converting the matte to blister copper and finally fire-refining to remove the oxidizable impurities and/or electrolytic refining to remove and recover the precious metal impurities in the copper. The major portion of the blister copper is electrorefined.

Traditionally, the smelters have been situated near the mines in order to minimize transportation costs for concentrates. At present, there are 18 primary smelters in the United States, thirteen of them west of the Mississippi. There are 16 electrolytic refineries which have traditionally been located near consumers on the East Coast where they account for about half of the electrorefining capacity. Recently some refineries have been built in the west near the smelters. Locations of U.S. smelters and refineries are shown in Figure III-2.

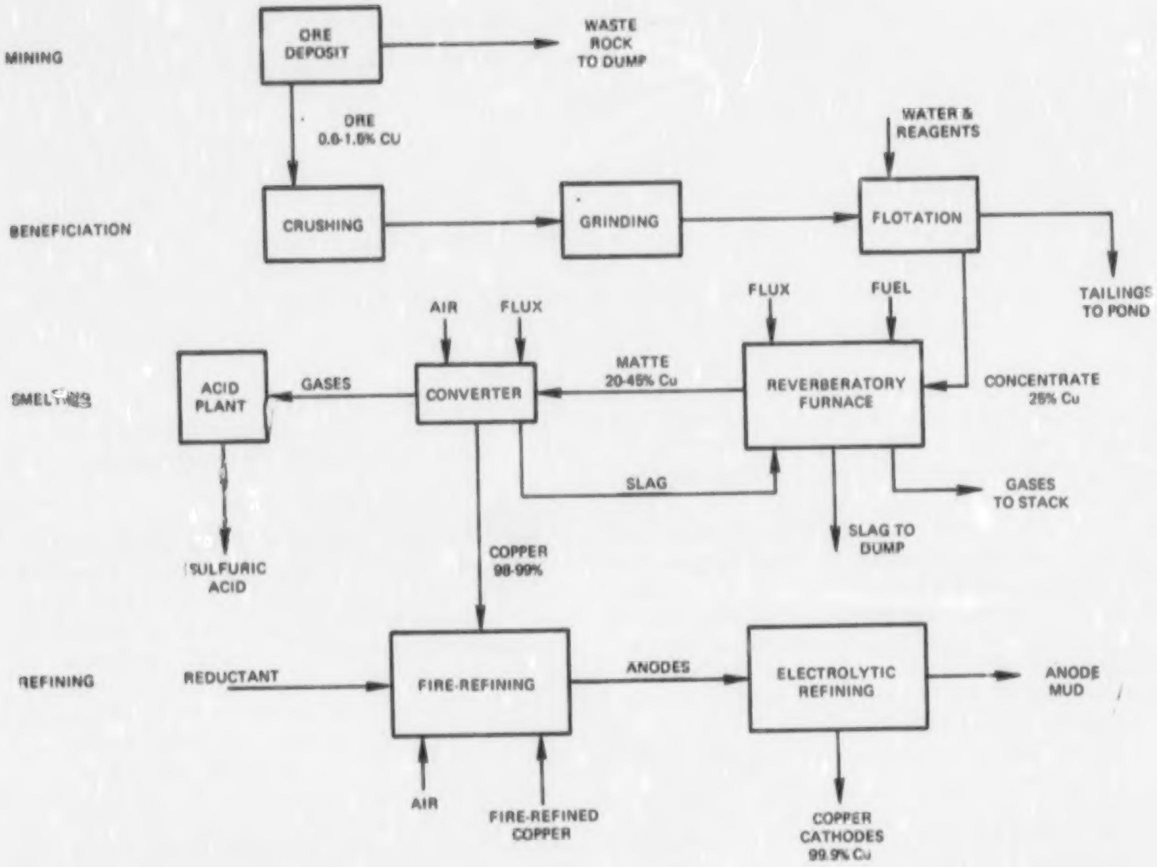
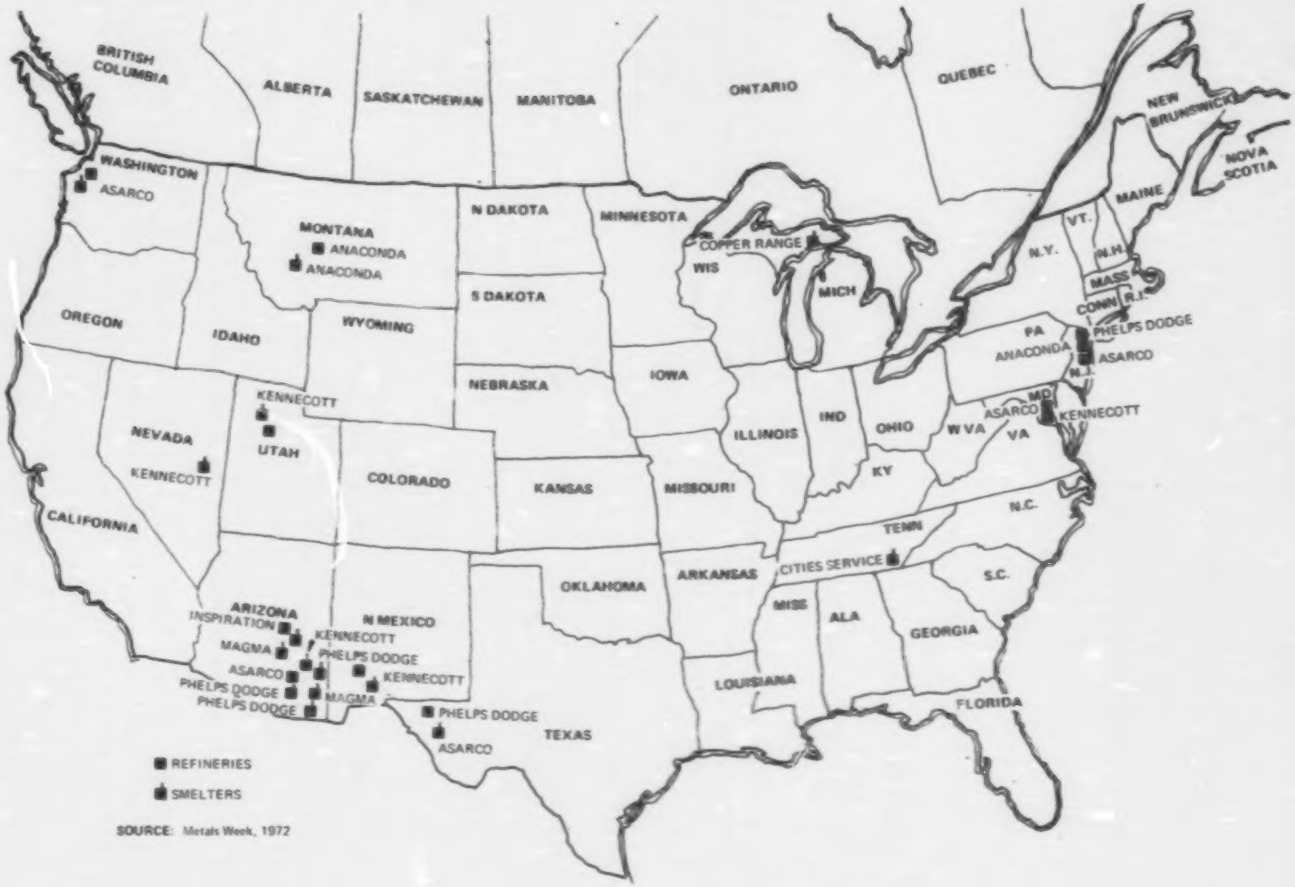

MINING
ORE DEPOSIT
WASTE ROCK TO DUMP
ORE 0.6-1.5% CU
WATER & REAGENTS
BENEFICIATION
CRUSHING
GRINDING
FLOTATION
TAILINGS TO POND
AIR
FLUX
FLUX
FUEL
SMELTING
ACID PLANT
GASES
CONVERTER
MATTE 20-45% Cu
REVERBERATORY FURNACE
CONCENTRATE 25% Cu
SLAG
GASES TO STACK
SLAG TO DUMP
SULFURIC ACID
COPPER 98-99%
REFINING
REDUCTANT
FIRE-REFINING
ANODES
ELECTROLYTIC REFINING
ANODE MUD
AIR
FIRE-REFINED COPPER
COPPER CATHODES 99.9% Cu

Figure III-1. Generalized Flowsheet for Copper Extraction From Sulfide Ores


BRITISH COLUMBIA
ALBERTA
SASKATCHEWAN
MANITOBA
ONTARIO
QUEBEC
NEW BRUNSWICK
NOVA SCOTIA
WASHINGTON
ASARCO
MONTANA
ANACONDA
ANACONDA
N DAKOTA
MINNESOTA
COPPER RANGE
WIS
MICH
MAINE
VT.
N.H.
N.Y.
MASS
CONN
R.I.
PHELPS DODGE
PA
ANACONDA
ASARCO
N.J.
MD
ASARCO
KENNECOTT
OREGON
IDAHO
WYOMING
S DAKOTA
NEBRASKA
IOWA
KENNECOTT
UTAH
NEVADA
KENNECOTT
COLORADO
KANSAS
MISSOURI
ILLINOIS
IND
OHIO
W VA
VA
KY
CALIFORNIA
N.C.
TENN
CITIES SERVICE
ARKANSAS
S.C.
OKLAHOMA
ARIZONA
INSPIRATION
KENNECOTT
MAGMA
PHELPS DODGE
ASARCO
PHELPS DODGE
PHELPS DODGE
MAGMA
N MEXICO
KENNECOTT
PHELPS DODGE
ASARCO
TEXAS
MISS
ALA
GEORGIA
LOUISIANA
FLORIDA
REFINERIES
SMELTERS

SOURCE: Metals Week, 1972

Figure III-2. Where the Smelters and Refineries are Located

Fabricating companies are the principal consumers of refined copper. They work the metal into semi-finished form such as sheet, strip, rod, tube, wire, and extruded or rolled shapes which are the raw materials for the manufacturing industries.

Although copper has many end uses, they can be classified into five broad categories:

1. Electrical/electronic equipment
2. Building construction
3. Transportation
4. Non-electrical industrial equipment, and
5. Ordnance.

Other applications include use in chemicals, inorganic pigments, jewelry, and coins.

Through subsidiaries or stockholdings, many large domestic producers operate foreign properties in both the developed and developing countries and are involved domestically in the production of other nonferrous metals such as aluminum, lead, and zinc. The financial posture of some of the companies has been changed by expropriation of certain foreign holdings, and nationalization in other countries continues to be a threat.

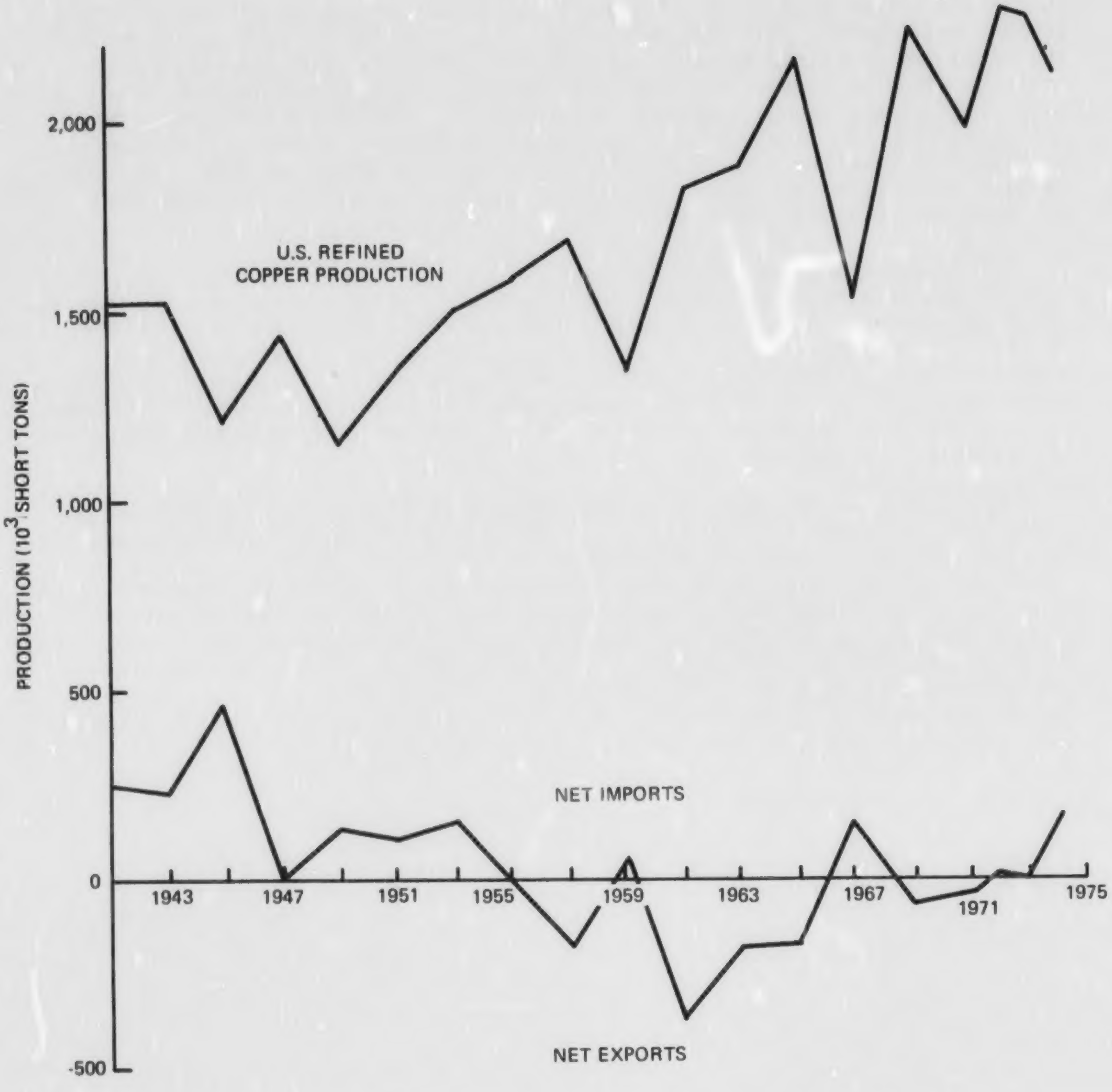
The domestic copper, lead, and zinc industries are interdependent to the extent that byproducts or residues from one industry form a part of the input to the other. The western copper, lead, and zinc industry is a significant producer of byproducts such as silver, gold, and bismuth. In certain instances, especially at the western lead smelters, the value of byproducts can equal or exceed that of the primary product--lead. In general, the byproduct supply and production is inelastic, i.e., not dependent on demand or price of the byproduct but dependent only on the primary metal production. Any factor (pollution-related or otherwise) that changes the output of the primary product would automatically affect byproduct output. An apparent exception might be the western lead smelter where, because of the high volume of coproducts, higher coproduct prices (e.g., silver, bismuth, etc.) can decrease the sensitivity of primary metal production to primary metal price.

An important aspect of the entire primary nonferrous industry is that traditionally the smelters and refineries have been operated as service operations at a fixed and relatively low profit margin which is not very sensitive to the price of the finished product. Hence, the impact of any change in price of the primary metal has to be reflected back and affects directly the value of the concentrate. In the 1960's, the traditional rule-of-thumb in determining concentrate value in the copper industry was to assume 4¢/lb for smelting charges and 5¢/lb for refining charges so that the value of copper contained in the concentrate was very approximately 9¢/lb below the cathode or wirebar market price. (The 1975 operating margin in the copper industry was about 16-18¢/lb.)

Because of this mechanism, any increase in smelting or refining costs cannot be "absorbed" by the smelter or refinery but can only be passed backward to the mine, and the net-back (the net concentrate value realized at the mine, e.g., smelter payment minus transportation costs) would be decreased. Should the market supply/demand constraints permit an upward adjustment in primary metal price, this increase would then be reflected back to the mine. The mechanism described above is of primary importance to custom and toll smelters since it is possible that a decreased concentrate value can result in mine closings and loss of smelter feed material. However, essentially the mechanism operates in the case of producers integrated from mining through smelting and refining since the concentrate transfer price is related to the primary metal price and again the mines would have to absorb the increased smelting and refining costs under adverse market conditions.

Given generally similar operating, tax, and pricing structures, and because of the overlap in company participation in copper, lead and zinc mining, smelting, and/or refining, the major companies are somewhat similar from the financial viewpoint. Sales and earnings of the primary nonferrous metals companies are cyclical. Major influences on earnings are the operating rate and metal prices. The latter fluctuate more than annual consumption or demand since prices tend to be sensitive to small imbalances between supply and demand and varying international situations.

Over the past 20 years, world consumption of copper has been increasing at an average annual rate of 4-4.5%. Despite competition from plastics and aluminum, copper consumption is expected to increase at about the same rate worldwide over the next decade with a slightly lower rate in the industrialized countries. The United States is a leading producer and consumer of primary copper, accounting for about one third of Free World production and consumption. Despite this, the United States has been in a position of undersupply since the early 1960's as shown in Figure III-3. Domestic mine production has been increasing recently at an adjusted rate of about 3.5% per year, while world mine production has been increasing at about 5% per year.



SOURCE: Arthur D. Little, U.S. Bureau of Mines, American Bureau of Metal Statistics.

Figure III-3. Trends in Net U.S. Imports and Production of Refined Copper

IV. COMPARISON OF CURRENT AND ALTERNATIVE PROCESSES

A. REASONS FOR CHOOSING OPTIONS TO BE ANALYZED IN DEPTH

1. Problems of Current Technology

The smelting technology in the United States evolved in a framework of low energy costs in locations distant from sulfuric acid markets and urban population centers. Thus the technology was not aimed at recovering sulfur values as sulfuric acid (as is the case abroad) and was not particularly efficient in its use of energy. Several changes have occurred in the past five years on the economic and regulatory scene which may influence the adoption of new technology for construction of new smelters or for switching to coal firing in existing reverbatory furnaces. These changes are as follows:

- Energy costs for smelting have increased rapidly. Cheap natural gas, the fuel used by most smelters, is not now available to the smelters particularly in peak demand months (winter) and might not be available at all in the future.
- Emissions of SO_2 to the atmosphere have to be controlled. After several years of debate, all issues relating to SO_2 emissions are yet to be resolved. These issues are as follows:
    - At present the New Source Performance Standards for primary copper smelters contains an exemption for reverbatory furnaces smelting "impure" concentrates (concentrates containing As, Sb, Bi, etc.). About 30% of the feed sulfur is emitted from the reverbs.
    - Emissions from streams containing high concentrations of SO_2 (converter and roaster gases) have to be controlled by technology such as sulfuric acid plants. Double absorption plants (or equivalent) are mandatory for new sources. This combination of uncontrolled reverbs but controlled roasters and converters can recover from about 50-70% of the sulfur in the feed in the form of sulfuric acid. New smelting technology can recover a larger fraction (over 90%) of the sulfur in the feed.

  - Federal Ambient Air Quality Standards which define permissible ground level concentrations of SO_2 have to be met at all times by a combination of permanent controls, e.g., acid plants, and production curtailment. The issue of when production curtailment should be used has not been resolved. The degree of permanent controls necessary to meet Ambient Air Quality Standards varies greatly with location. The control of roaster or converter emissions is adequate for meeting Ambient Air Quality Standards only in certain locations.

  - Compared to the cost of SO_2 control, the costs of complying with other existing pollution control legislation, e.g., water and solid wastes, is quite small. However, this situation could change as new standards are proposed for controlling emissions of other substances.

- The acid produced by smelters cannot be economically transported to traditional acid markets, and it has to be disposed of (by selling it at a low price) in the general vicinity of the smelter. This resulting availability of low-priced acid in the west has made it possible to use it to make wet-process phosphoric acid from low grade western phosphate rock or to use it to leach mine dumps and low grade deposits of copper ore which cannot be treated conventionally for the extraction of the contained copper. An alternative is its neutralization with limestone. This is being practiced indirectly on copper ores high in limestone.

- Copper smelting and refining have been capital intensive in the past, and the capital intensity has increased significantly in recent years because of pollution control requirements and inflationary pressures. Also, pyrometallurgical operations involved significant economies of scale, and the smallest economic size is over 100,000 ton/yr of copper. Because of the small growth rate in copper consumption, an increment in capacity of 100,000 ton/yr or more for any United States company implies significant risk since their market share would have to increase by 20% or more. This is why smelting and refining capacity has generally increased by modifications of existing plants rather than by the construction of new plants in remote locations. We believe that the New Source Performance Standards will affect this traditional mode of capacity expansion since emissions from the new portion of the plant may require different treatment in order to comply with New Stationary Source Performance Standards.

2. Reasons for Choosing Options for Detailed Analysis

We selected an illustrative group of process changes which we believe are likely to be implemented by the U.S. industry in the near term. The set of process changes is not exhaustive but is representative of industry responses to one or more of the problems described above in Section 1.

The topics selected for detailed analysis are:

- New smelting processes
  - Outokumpu flash smelting
  - Noranda process
  - Mitsubishi process
- The use of oxygen in smelting
- Slag cleaning processes
- Arbiter process

The first three are illustrative of new high-intensity pyrometallurgical processes. The use of oxygen in smelting, particularly in the context of these new processes, is an interesting development in that it not only decreases net energy use but also increases smelting intensity. The latter can significantly decrease the capital cost of a smelter per unit of output. The slag cleaning processes (flotation and electric furnace cleaning) are important adjuncts to the new processes since these processes would not be economically viable unless residual copper (up to 12%) in the slag was recovered. The Arbiter process is the earliest of several hydrometallurgical processes being adopted for the extraction of copper from sulfide concentrates. These processes produce cathode copper directly and release sulfur from the concentrates in forms other than SO_2. It is feasible to build plants sized around 40,000 tons of copper per year at a unit cost of about $1000/annual ton of copper, which is about the same as the unit cost of a large (over 100,000 ton/yr) copper smelter and refinery. However, such a hydrometallurgical process does not offer significant economies of scale, and larger plants would require the same unit capital investments.

The sections that follow discuss the base line and the process options. Background literature references used in evaluating each process are given at the end of the report.

B. BASE LINE: CONVENTIONAL SMELTING AND REFINING

1. Introduction

Conventional smelting and refining is the base line against which potential process alternatives have been compared in order to evaluate pollutional and energy consequences of these process alternatives.

Conventional smelting of sulfide concentrate involves the smelting of concentrates in the reverberatory furnace (reverb) either directly (green charge smelting) or after roasting (calcine smelting). The mixture of molten sulfides from the reverb is converted to blister copper in converters. A detailed description of conventional smelting is presented in Appendix A. Both green charge and calcine smelting form the base line for comparison of other new smelting approaches since both approaches are widely used in the United States.

Conventional electrorefining (also described in Appendix A) purifies the smelter output to cathode quality copper. We have used smelting plus refining as the base line for comparison of the Arbiter hydrometallurgical process since it produces cathode copper directly from concentrates.

2. Effluents

Figure IV-1 is a schematic flow diagram of the conventional smelting and refining process. The emission sources of pollutants are shown in four categories: air, solid, water, and fugitive. The latter are air emissions that come from diffuse sources. Table IV-1 shows the magnitude of these streams and the major constituents.

a. Air Pollution

(1) Current Methods

At present, there are three methods in use at copper smelters for reducing the sulfur dioxide concentrations in the vicinity of a smelter. These are: the use of a tall stack to disperse dilute gas streams; the production of sulfuric acid by the contact process from concentrated gas streams to achieve a degree of reduction in emissions; and production curtailment.

The tall stack discharges sulfur dioxide at such heights that the gas is diluted when dispersed into the lower atmosphere. It is possible to add preheated air into the stack to achieve additional dispersion and dilution. Because tall stacks and preheated air can achieve dispersion and dilution when used in conjunction with other means of limiting emissions, there is no simple relationship which can predict ambient concentrations as a function of percent sulfur recovery. The overall control strategy has to be well defined, and local weather patterns have to be considered.

The contact sulfuric acid process is well established for treating SO_2-containing off-gases from metallurgical plants. Modern contact acid plants require at least 4.5-5% sulfur dioxide in the feed gas in order to operate autogenously (i.e., without external heat). For handling lower concentrations of SO_2, an additional fuel input is required. The acid plant size is primarily a function of the volume of gas handled. Hence, for a constant acid output, an acid plant operating on more dilute gases is much larger (and more expensive) than an acid plant operating on more concentrated gases. With the currently used vanadium pentoxide catalysts, the upper level of SO_2 concentration in the feed gas to an acid plant is between 7% and 9%. Gas streams more concentrated than this require dilution.

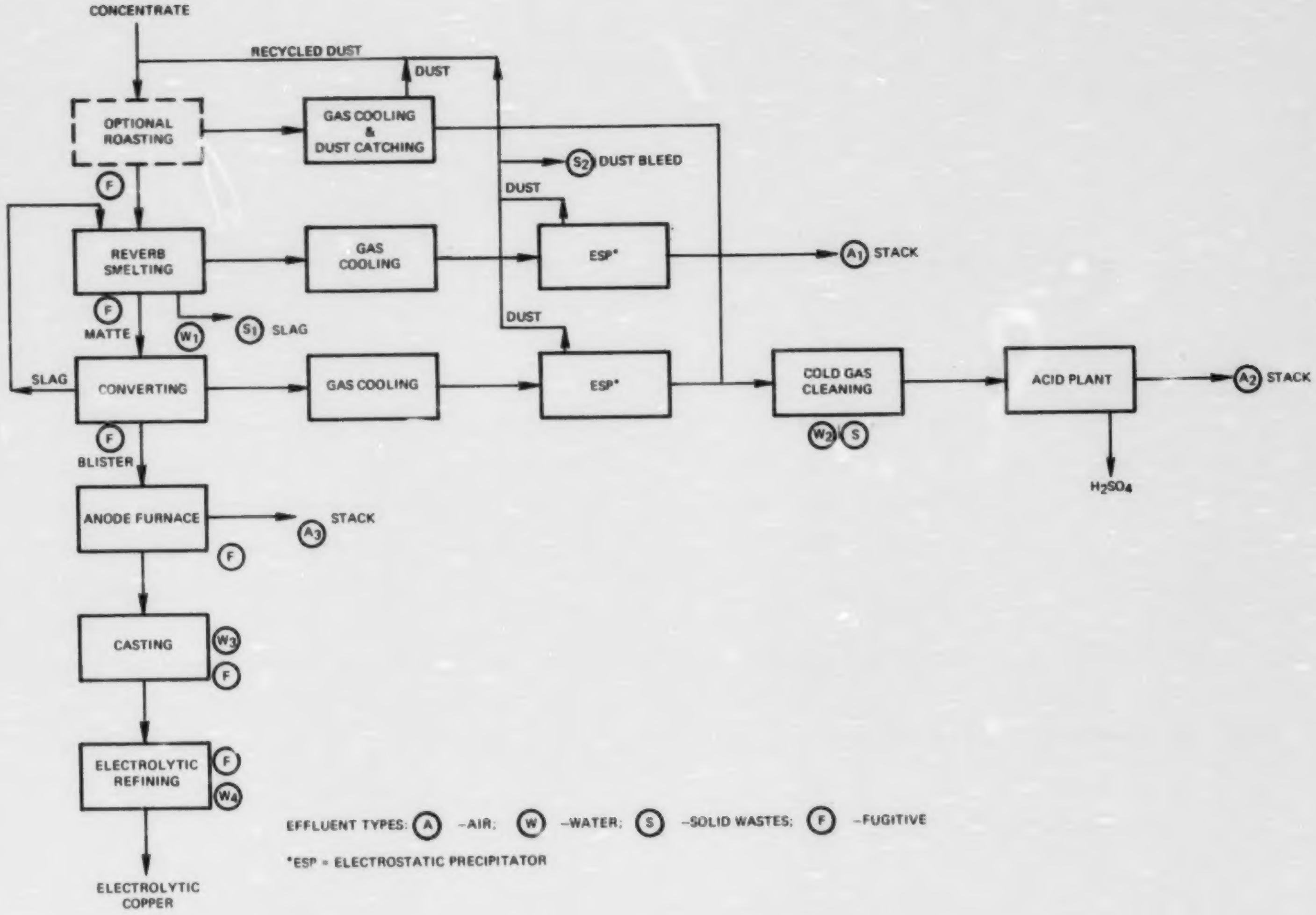

CONCENTRATE
RECYCLED DUST
DUST
OPTIONAL ROASTING
GAS COOLING & DUST CATCHING
S_2 DUST BLEED
DUST
F
REVERB SMELTING
GAS COOLING
ESP*
A_1 STACK
F
MATTE
W_1
S_1 SLAG
DUST
SLAG
CONVERTING
GAS COOLING
ESP*
COLD GAS CLEANING
ACID PLANT
A_2 STACK
W_2 S
H_2SO_4
F
BLISTER
ANODE FURNACE
A_3 STACK
F
CASTING
W_3
F
ELECTROLYTIC REFINING
F
W_4
ELECTROLYTIC COPPER
EFFLUENT TYPES: A -AIR; W -WATER; S -SOLID WASTES; F -FUGITIVE
*ESP = ELECTROSTATIC PRECIPITATOR

Figure IV-1. Sources of Emissions in Conventional Copper Smelting and Refining

TABLE IV-1

EMISSIONS FROM CONVENTIONAL SMELTING

Stream	Stream Size	Major Constituents
• Air Pollution		
A-1 - Reverb Gas	82,000 scfm	SO_2: 1-2%; O_2: 5%; Particulates: 50 $\mu g/NM^3$
A-2 - Acid Plant Tail Gas	38,800 scfm	SO_2: 0.2%
A-3 - Anode Furnace Gas	NA	Flue Gas, Some SO_2
• Water Pollution		
W-1 - Slag Granulation	1200 gal/ton	TDS, SSS
W-2 - Acid Plant Blowdown	340 gal/ton	TDS, TSS, Acidity
W-3 - Contact Cooling	180 gal/ton	TDS, TSS
W-4 - Black Acid Bleed	17 gal/ton	Acidity, TDS, TSS
• Solid Wastes		
S-1 - Reverb Slag	3 ton/ton Cu	Iron Silicates
S-2 - Dust Bleed	0.3 ton/ton Cu	Copper Oxides, Minor Elements

The third method for controlling sulfur dioxide concentrations at ground level is production curtailment when adverse weather conditions prevail. This method has been referred to as "closed loop control" or a Supplementary Control System (SCS) when it is based on the monitoring of sulfur dioxide concentrations at ground level at various sites in the areas surrounding the smelter and using this information to control the smelter operating rate. When ground level concentrations increase as a result of adverse weather conditions, the smelter operation is curtailed to reduce the emission rate.

(2) Sulfur Emission Source in a Conventional Smelter

With over 30% sulfur, most copper concentrates contain more sulfur than copper. About 1-2% of the sulfur entering the smelter is lost in the slag and perhaps 3-4% evolves as fugitive emissions. The remaining sulfur is in gaseous effluents from roaster, reverb, and converters. Typical sulfur distributions in conventional smelting are:

Sulfur Distribution (%)

Source	Calcine Smelting	Green Charge Smelting
Roaster	20	-
Reverb	25	40
Converter	50	55
Slag and Fugitives	5	5
Total	100	100

As mentioned in the previous section, the conventional smelting process evolved in geographical areas where acid markets were unavailable and where all SO_2-containing gas streams were vented to the atmosphere (after particulate control, if necessary). Thus, conventional technology uses gas-handling techniques (e.g., use of dilution air for cooling of gas streams) which would not be used if the stream were to be treated for SO_2 recovery. However, streams from the roaster and converter can be handled to minimize air leakage. This results in SO_2 concentrations over 4-5% which is adequate for autogenous sulfuric acid manufacture -- the most cost-effective control technology for removing SO_2 from such streams. The reverb gases are a high volume (up to 100,000 scfm) and low concentration (0.5-2% SO_2) stream, not amenable to autogenous sulfuric acid manufacture and have to be discharged via tall stacks. EPA's work during the promulgation of New Stationary Source Standards showed that SO_2 control of reverb emissions was not economically feasible. (This aspect is discussed further in the next section.)

With conventional smelting as well as with the new smelting processes, SO_2 control is achieved via an "end-of-pipe" treatment facility, i.e., a sulfuric acid plant. Changes in processing and in gas handling and gas cooling are necessary, and no clear delineation is possible between process units and pollution control units. For this reason, we have integrated the costs of SO_2

control into the calculation of operating costs for both the base line as well as the new smelting process options. Furthermore, the base line case assumes control of converter gases alone (equivalent to about 50% sulfur control) and no control of reverb gases since this is typical of conventional smelting operations today. The process options considered later do not incorporate reverbs and recover more SO_2 than the base line. This is somewhat unique among the various industries studied.

Table IV-2 shows how one would calculate the price of sulfuric acid manufacture if it was a separate entity receiving the off-gases from converting furnaces. Converter gases fluctuate in volume and quality because converting is a batch operation. For smaller smelters, the acid plant has to be oversized to accommodate these fluctuations; and the cost of air pollution control can be more than what is shown in Table IV-2.

The reverb gas contains particulates in addition to SO_2. Technology is presently available (electrostatic precipitators) which will usually permit meeting the particulate emission levels established for copper smelters.

Electrolytic refineries have no air pollution problems.

The addition of an acid plant substantially increases the power demand at a smelter. Without acid plants, most smelters generate more than adequate power for their internal needs from the waste-heat boilers on the reverberatory furnaces and power generation can be increased by installing waste-heat boilers to cool the hot converter gases. With acid plants, smelters become net purchasers of power.

Increasing sulfur capture by control of reverb gases requires scrubbing or SO_2-concentration technology. Data published by the EPA* suggest that the costs of this technology are very high. For example, the production of sulfuric acid from roaster and converter gases costs about $70-80/ton of sulfur. The recovery of sulfur from reverb gases via scrubbing or SO_2-concentration costs in the range of $200-300/ton of total sulfur removed and $400-500/incremental ton of sulfur recovered via the scrubbing or concentration techniques. For this reason, EPA has concluded that control of reverb gases is not economically achievable.

b. Solid Wastes

Slightly more than three pounds of solid waste per pound of pure copper are generated in a copper smelter. These come in the form of a slag and collected flue dust.

(1) Slag

The converter slag is recycled to the reverb in order to recover its copper content. The slag tapped from the reverberatory furnace (and granulated in some cases) is disposed of as an inert rock. Reverb slag is mainly an iron silicate, containing about 0.5-0.9% copper and minor elements in rather dilute form. It is sent to landfill at an estimated cost of $5/ton of slag, or $15/ton of copper produced.

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* Background Information - New Source Performance Standards for Primary Copper, Zinc, & Lead Smelters, EPA, Office of Air & Water Programs, August 1973.

TABLE IV-2

COSTS OF OPERATING AN ACID PLANT: CONVENTIONAL SMELTING

Basis: 52,000 scfm
8% SO_2 Concentration
800 ton/day of Acid
330 Operating Days/Yr

Capital Investment (CI):	$\$10^6$
Waste heat boiler	2.13
Electrostatic precipitator & cold gas cleaning	1.06
Double Absorption (DA) acid plant	12.88
Total	16.07

Expected H_2SO_4 Production Cost:	$/Yr	$/Yr
Variable Costs		
Direct Operating & Maintenance Labor 13 men @ $5.75/hr, 48 hr/week (L)	188,370	
Supervision @ 15% of Labor (S)	28,255	
Overhead @ 35% of Labor & Supervision	75,818	
Total Labor		292,433
Operating & Main. Supplies @ 2.4% of Cap. Cost	385,680	
Misc. Supplies	29,200	
Total Supplies		414,880
Energy - Fuel oil 4,550 bbl @ $11.60/bbl	52,780	
Electricity 180 kWh/ton @ $0.021/kWh	997,920	
Total Energy		1,050,700
Other expenses - shutdown		255,000
Total Variable Costs		2,012,823
Fixed Costs		
Plant Overhead @ 65% (L + S)		140,807
Local Taxes & Insurance @ 2% of CI		321,400
Depreciation 14 years, straight line		1,147,857
Total Fixed Costs		1,610,064
Total Variable & Fixed Costs		3,622,887
ROI 20% of CI		3,214,000
Total charge against H_2SO_4 manufacture		6,836,887
Total Charge/Ton of acid		$25.90

(2) Flue Dust

The flue dusts result from entrained particles and condensed effluents in the gas stream. Typically, 3-6% of the total weight of solids entering the smelter are evolved as dust. Coarse particles are caught in the cooling chambers, while fine particulates are removed by electrostatic precipitators operating slightly above the dew point of the gas stream. While the electrostatic precipitator is highly efficient, the fumes from volatile metal species can still be present in the gas stream. For example, the converter gases are usually scrubbed after the initial particulate removal in order to further reduce the concentration of minor elements which could create problems in the operation of a sulfuric acid plant.

All flue dusts contain entrained copper, and they are mostly recycled to the reverberatory furnace. They may also contain volatile impurities in a concentrated form. Excessive impurity build-up by dust recirculation would impair the quality of the blister copper. At times, it is economical to process these dusts further in order to recover such metals as zinc, lead, etc. Depending on the composition of the feed, a fraction of the dust generated may be diverted and either sold to other specialized smelters which recover the contained metals or encapsulated for safe disposal. For example, encapsulation could be accomplished by incorporating the dust into a matrix such as a pozzolanic cement which is suitable for landfilling. To the best of our knowledge, some dust has been stockpiled at certain smelters but none has been added to a pozzolanic cement.

c. Fate of Minor Elements

A schematic diagram of the flows of minor elements in a copper smelter is shown on Figure IV-2, and a breakdown is shown in Table IV-3. Impurities are eliminated from the copper-rich stream by slagging and volatilization, whereas they are diluted in the slag by the inert oxides such as Fe_2SiO_4. The amount of dust recirculated is therefore a key factor in the steady-state flow of impurities. This is why the data in Table IV-3 show the distribution of impurities on the basis of the total feed to the reverb rather than the impurities in the ore concentrate only.

In quantifying these streams, the scarce data available from published literature have been supplemented by our "best engineering judgment." Due to the immense variety of possible concentrates and operating practices, these numbers should be considered as "order of magnitude" values only.

The impurities remaining in the blister copper (other than sulfur and oxygen) are carried over to the refining where they distribute themselves among:

- the final product;
- the anode slimes, which are further processed for precious metals recovery; and
- the electrolyte, from which nickel may be separated.

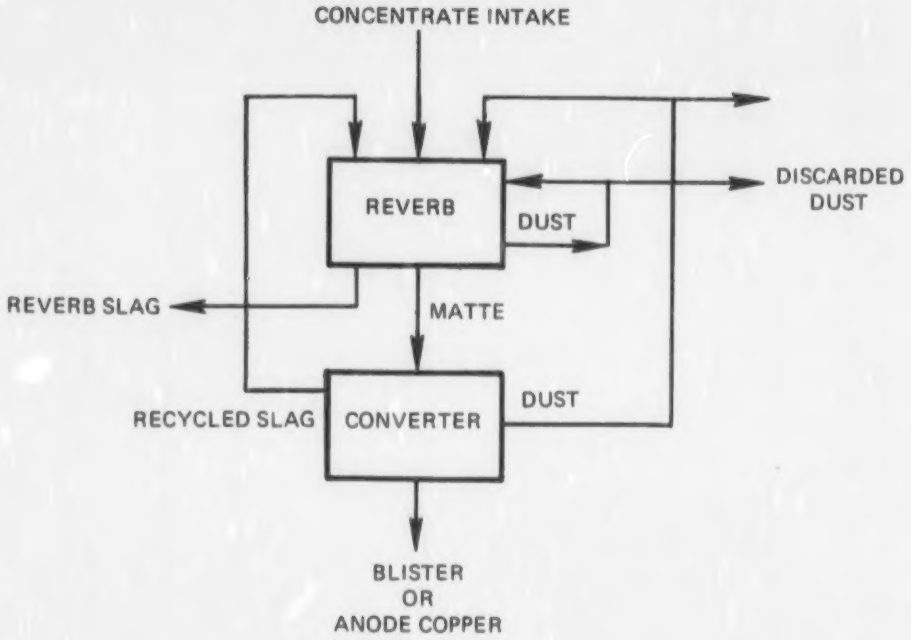

CONCENTRATE INTAKE
REVERB
DUST
DISCARDED DUST
REVERB SLAG
MATTE
RECYCLED SLAG
CONVERTER
DUST
BLISTER OR ANODE COPPER

Figure IV-2. Diagram of Impurity Flow Within a Copper Smelter

TABLE IV-3

SUMMARY OF THE WEIGHT DISTRIBUTION OF MINOR ELEMENTS IN THE CONVENTIONAL SMELTING PROCESS (MATTE GRADE = 40% COPPER)

Element	Total Input to the Reverb (1)	Granulated Reverb Slag	Total Reverb Dust and Volatiles	Estimated Reverb Emissions (2)	Total Converter Dust (3)	Remaining in Blister Copper
As	100	54	12	<0.12	25	5
Sb	100	54	16	<0.16	14	9
Bi	100	8	85	<0.85	6	1
Hg	100	0	≈100	≈100	0	0
Pb	100	10	80	<0.80	10	traces
Zn	100	30	60	<0.60	10	traces
Se	100	<10	<10	<0.10	>45	>45
Te	100	<10	<10	<0.10	>45	>45

Notes:

(1) Recycled converter slag, recycled dusts and new ore concentrate are the contributors to this total input.

(2) Estimated reverb emissions are that fraction of total reverb dust not captured by electrostatic precipitators.

(3) The converter dust is captured in electrostatic precipitators. The residual fines are captured in the wet scrubbers preceding the acid plant and constitute less than 1% of the total converter dust.

Source: Arthur D. Little, Inc. estimates

d. Water Pollution

The primary copper industry must control water emissions from three major sources, the mines, the smelters, and the refineries. In controlling water pollution it is often necessary to remember that in controlling the air pollution problems, a water pollution problem can be created since some of the most effective air pollution technologies are based on the use of water in scrubbing. Furthermore, the water drainage problem from tailings disposal areas is of considerable concern to the industry, but much less than in the coal mining industry. Although air and water pollution control have been considered separately, it is mandatory that in arriving at solutions to one problem, another one of equal or greater magnitude is not created.

The water pollution regulatory constraints on the copper industry arise mainly as a result of Sections 304(b) and 306 of the Federal Water Pollution Control Act Amendments of 1972. Under this Act, the EPA has conducted technical studies which are published as "Development Documents" and form the basis for the Effluent Limitation Guidelines. These guidelines refer to three specific discharge levels.

- Best Practicable Control Technology Currently Available (BPCTCA) - to be met by industrial discharges by 1977.
- Best Available Technology Economically Achievable (BATEA) - to be met by 1983.
- New Source Performance Standards (NSPS) - to be applied to all new facilities constructed after the promulgation of these guidelines.

In order to achieve the effluent limitations, the recommended treatment technology for the copper industry must perform three functions:

- remove suspended solids,
- adjust pH, and
- remove the specific heavy metals.

To perform these functions, the following treatment steps are recommended:

- lime precipitation,
- settling, and
- pH adjustment.

Since all of the heavy metals included in the proposed effluent limitations have very low solubility in the alkaline pH range, the addition of lime causes the metals to precipitate out of solution as hydroxides and carbonates. The metal precipitates, along with other suspended solids present in the wastewater, are separated from the wastewater stream by means of settling and are withdrawn as a sludge. Since the wastewater is still at a high pH after this step, it is necessary to lower the pH by injecting carbon dioxide gas or other acid into the water. This step is usually performed in a separate basin. Other recommended techniques for improving the effectiveness of the previously mentioned end-of-pipe treatment are:

- reuse of water in other operations;
- control of mine water drainage by modification of mining techniques, construction of diversion structures, or ditching; and
- use of solar evaporation to eliminate the discharge of excess water.

In a copper smelter and refinery the sources of wastewater are:

- slag granulation (if this is practiced);
- acid plant blowdown (i.e., blowdown from wet scrubbers ahead of the acid plant);
- metal cooling;
- spent electrolyte and washings; and
- storm water commingling with process wastewaters.

Table IV-4 shows raw waste characteristics.

The Effluent Limitation Guidelines for primary smelters and refineries in net evaporation areas is zero discharge of process wastewater pollutants, based on recycle, reuse, and solar evaporation. This standard applies to both the 1977 (BPCTCA) and 1983 (BATEA) guidelines. (The applicability of this standard to a particular smelter has been challenged in court.) We have used the zero discharge standard as applicable in all cases since we have assumed that the new process options would probably be utilized in the Southwestern United States, e.g., Arizona, where net evaporation occurs.

Zero discharge is achieved by:

- neutralization of acidic streams;
- settling (thickening) of streams containing suspended solids;
- cooling of contact cooling water for recycle, and
- solar evaporation from storage areas.

Furthermore, any blowdown from these systems is bled into the water recycle system of a nearby mill. The costs of water pollution control are estimated to be $3.25/ton as shown in Table IV-5.

TABLE IV-4

RAW WASTE CHARACTERISTICS OF CERTAIN STREAMS IN COPPER SMELTING (TYPICAL VALUES)

(gal/lb)

Parameter	Slag Granulation Water	Acid Plant Blowdown	Anode Casting
pH	0.091	0.024	0.09 - 0.1
TDS	0.588	2.94	0.212
TSS	0.240	0.023	0.004
$SO_4^=$	0.069	0.431	0.003
CN^-	-	-	-
As	0.0022	0.002	-
Cd	-	0.0001	-
Cu	0.0017	-	-
Fe	-	0.0005	-
Pb	0.0015	0.0010	-
Hg	-	-	-
Ni	-	-	-
Se	-	0.0001	-
Te	-	-	-
Zn	0.0077	0.0026	-
Oil and Grease	-	-	-
Flow/Production	599.20*	176.17**	7.35 - 93.48***

* 1200 gal/ton
** 35 gal/ton
***15-180 gal/ton

Source: EPA Development Document - EPA 440/1-75/032-b

TABLE IV-5

ESTIMATED WATER POLLUTION COSTS - COPPER SMELTING

Basis: 100,000 ton/yr
Estimated Capital Investment: $500,000

	$/yr
Direct Operating Costs	
Labor and Supervision - 3,000 hr @ $14.75/hr	$ 44,000
Electricity - 0.9 x 10^6 kWh @ $0.021 kWh	19,000
Lime - 1,500 tons @ $35/ton	52,000
Maintenance (4% of Investment/year)	20,000
Sludge Disposal - 9,000 tons @ $5.00/ton	45,000
	$180,000
Fixed Operating Costs	
Local Taxes and Insurance - 2% of Investment	$ 10,000
Depreciation (7%)	35,000
Return on Investment (20%/yr)	100,000
Total Fixed Operating Costs	$145,000
Total Operating Costs	$325,000
Unit Costs ($/ton Copper)	$3.25

3. Economic Factors

a. Smelting

Table IV-6 shows estimates of capital and operating costs for conventional smelting based on data in the literature, e.g., Schwartz (1975), Foard and Beck (1971), and our files. The raw material and energy costs are representative of the Southwest, e.g., Arizona.

It should be noted that the costs in Table IV-6 are for a "typical" chalcopyrite concentrate in a "typical" location. They have been derived on a basis consistent with the costs shown later to be "typical" of the new processes. Thus, these costs are for comparison purposes to evaluate the advantages of new technology. They should not be interpreted as current costs of actual smelters in Arizona.

TABLE IV-6

OPERATING COSTS: CONVENTIONAL SMELTING

(Basis: Copper sulfide concentrates, 28.6% Cu, 29.3% Fe, 33.4% S; 100,000 ton/yr of anode copper)

			Greenfeed Smelting		Calcine Smelting	
	Unit	$/Unit	Units/ Ton	$/Ton Cu	Units/ Ton	$/Ton Cu
CAPITAL INVESTMENT (CI) $/annual ton Cu			$650		$750	
OPERATING COSTS						
VARIABLE COSTS						
Silica Flux	ton	8.00	1.14	9.12	1.14	9.12
Limestone	ton	10.0	0.14	1.40	0.14	0.40
H_2SO_4 Credit	ton	10.00	1.93	(19.30)	2.45	(24.50)
Fuel Oil	10^6 Btu	2.00	22.7	45.40	18.60	37.20
Natural Gas	10^6 Btu	0.65	1.3	0.85	1.3	0.85
Electricity	kWh	0.021	347.00	7.29	441.00	9.26
Water: Process	10^3 gal	0.20	1.06	0.21	1.06	0.21
Cooling	10^3 gal	0.05	2.0	0.10	2.0	0.10
Refractories	ton	300.00	0.01	3.00	0.01	3.00
Direct Operating and Maintenance Labor (L)	man-hr	5.75	6.2	35.65	6.5	37.38
Supervision (S)	L	15% L	---	5.35	---	5.61
Maintenance Materials	CI	4% CI	---	26.00	---	30.00
Labor Overhead	L+S	35% (L+S)	---	14.35	---	15.04
TOTAL VARIABLE COSTS				129.42		124.67
FIXED COSTS						
Plant Overhead	L+S	65% (L+S)	---	26.65	---	27.94
Local Taxes & Insurance	CI	2% CI	---	13.00	---	15.00
Depreciation	CI	7% CI	---	45.00	---	52.50
Capital Recovery	CI	20% CI	---	130.00	---	150.00
TOTAL FIXED COSTS				215.15		245.44
TOTAL COSTS				349.57		370.11

The following should be noted:

- The operating costs exclude concentrate costs. This is consistent with the concept of a smelter's "operating margin" where the spread between the copper price and concentrate value is relatively constant and independent of the copper price.

- The concentrates are assumed to contain no precious metals or impurities. Many concentrates contain one or the other or both. The smelter margin is improved by overrecovery of precious metals, i.e., the difference between metals recovered and metals paid for. It might also be improved by penalties assessed for impurities in the concentrates. In consideration of generalized processing approaches, the usual industry practice is to ignore these factors.

- Copper overrecovery is not included. For all of the pyrometallurgical processes under consideration, it would amount to about $15/ton copper.

- Fuel oil is the fuel selected for the smelting furnace. Any fuel (pulverized coal or natural gas) can be used instead. Natural gas is used for "poling" (reducing oxygen in anode copper).

- Sulfuric acid has been credited at $10/ton, which is a reasonable "disposal" price for this acid in the Southwest. As discussed later, this does not cover the cost of producing this acid.

- The net energy requirements involve the use of waste heat recovery equipment for cooling hot gases. Typically, a reverb will recover about 1.2 to 1.3 x 10^6 Btu/ton of charge. Since all recovered energy is used within the plant, a waste heat credit is not shown.

- The costs include the costs of meeting Federal Ambient Air Quality Standards for SO_2 and particulates and the Effluent Limitation Guidelines for 1983 for water pollution for existing plants, which are the same as the Guidelines for New Sources.

- The total operating costs are about 17-18¢/lb with direct costs of about 5-7¢/lb depending upon whether acid credit is included. These compare with custom smelter charges (at existing older facilities) of approximately 9-11¢/lb for smelting alone.

Table IV-7 shows pollution control costs. Out of the total operating costs of 17-18¢/lb copper shown in Table IV-6, pollution control costs amount to about 3¢/lb.

TABLE IV-7

COST OF POLLUTION CONTROLS IN CONVENTIONAL SMELTING

Basis: 100,000 Short Tons of Copper/Yr

			Green Feed Smelting		Calcine Smelting	
	Unit	$/Ton	Units/Ton	$/Ton Cu	Units/Ton	$/Ton Cu
Acid Manufacture	Ton	25.90	1.93	49.99	2.45	63.46
Credit from Acid Sale	Ton	(10.00)	1.93	(19.30)	2.45	(24.50)
Slag Disposal	Ton	5.00	3	15.00	3	15.00
Water Pollution Control*				3.25		3.25
Dust Disposal(1)	Ton	24.00	0.02	0.48	0.02	0.48
Total Smelting				49.42		57.68

---

*See Table IV-5

(1) The amount of dust bled and disposed depends on the quality of the feed. It was taken here as 10% of the total dust emissions (assumed to be 5% of the total charge to the smelter).

Source: Arthur D. Little, Inc. estimates

b. Electrorefining

Table IV-8 shows estimates for electrorefining anode copper to cathode copper. Most refineries melt and cast cathode copper to other shapes or products. We have selected cathode copper as a basis in order to provide a basis for comparison for hydrometallurgical processes which also produce cathode quality copper. It should be noted that about 15% of anode copper is returned as anode scrap for remelting and casting.

Electrolytic refineries have only one major effluent stream -- spent electrolyte. The treatment costs for neutralization and disposal of this stream are estimated to be about $0.50/ton of copper.

TABLE IV-8

OPERATING COSTS: CONVENTIONAL ELECTROREFINING
(Basis: 100,000 ton/yr cathode copper; 15% anode scrap recycle)

	Unit	$/Unit	Units/Ton	$/Ton Cathode Cu
CAPITAL INVESTMENT (CI) $/annual ton			$450	
OPERATING COSTS				
VARIABLE COSTS				
Sulfuric Acid	ton	10.00	0.01	0.10
Fuel Oil	10^6 Btu	2.00	2.00	4.00
Electricity	kWh	0.021	250.00	5.25
Water: Process	10^3 gal	0.20	1.00	0.20
Direct Labor (L)	Man-hr	5.75	6.00	34.50
Supervision (S)	L	15% L	---	5.18
Maintenance Materials	CI	4% CI	---	18.00
Labor Overhead	L+S	35% (L+S)	---	5.95
TOTAL VARIABLE COSTS				73.18
FIXED COSTS				
Plant Overhead	L+S	65% (L+S)	---	25.79
Local Taxes & Insurance	CI	2% CI	---	9.00
Depreciation	CI	7% CI	---	31.50
Capital Recovery	CI	20% CI	---	90.00
TOTAL FIXED COSTS				156.29
TOTAL COSTS				229.47

C. OUTOKUMPU FLASH SMELTING

1. Flash Smelting - Concept and Operations

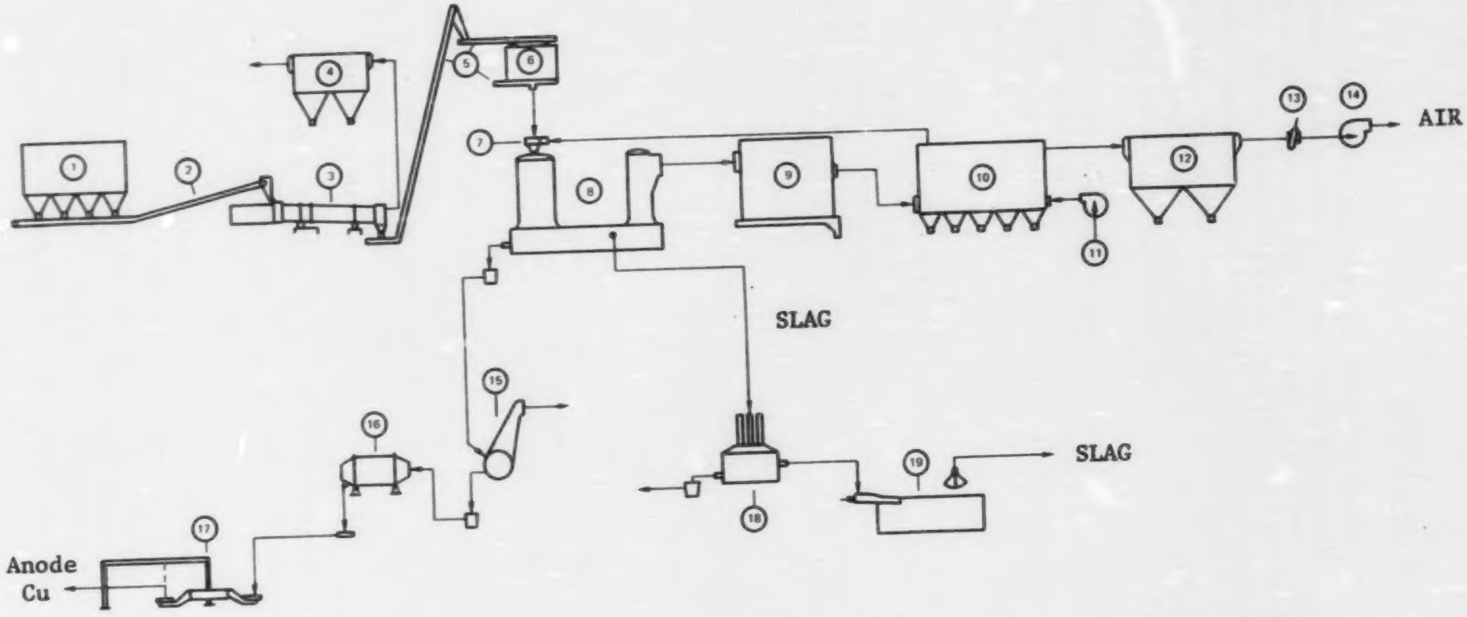
Flash smelting combines the separate roasting and smelting operations of conventional copper extraction into a combined roasting-smelting process. The heat generated by the exothermic roasting reactions can be used for smelting so that little or no extraneous fuel is needed. A characteristic of this method is that fine-grained concentrates are used and the smelting takes place in suspension, which allows for rapid reaction rates. The major advantages of the method are a reduction in fuel used for smelting and the production of a stream of gas high in SO_2 which is suitable for sulfuric acid manufacture.

In the late 1940's Outokumpu Oy of Finland developed the flash smelting process, and has been using this process at its Harjavalta works since 1949. Other flash smelting techniques have been developed, e.g., oxygen flash smelting in Canada, cyclone smelting in Russia. Of these, only the Outokumpu approach has been adopted widely in other parts of the world.

The processing of copper concentrates by flash smelting at the Harjavalta works of Outokumpu is shown in Figure IV-3. From storage, the feed materials (concentrates and silica sand) are fed by automatic weighers in the right proportions onto a belt which conveys the charge to a drier. In the drier, which is a direct oil-fired rotary kiln, the concentrate is thoroughly dried. The finest particles leave the kiln as flue dust but are collected in an electrostatic precipitator (ESP) and returned to the main concentrate flow. The charge is transported by means of a pneumatic elevator to the feed hopper. From the feed hopper, the dried charge is fed by a conveyor into the concentrate burner. In the concentrate burner the charge is mixed with preheated air at about 930°F. It reacts in the reaction shaft (the portion of the flash furnace beneath the concentrate burner) and the temperature rise is enough to melt the particles. The molten particles are separated from the gas phase in the settler (the horizontal portion) thus forming matte and slag. The matte grade is controlled by the air/concentrate ratio.

From the uptake, the gases are led into a waste heat boiler - a forced circulation type of water wall radiation boiler. The main function of the radiant section of the boiler is to cool the gas containing molten dust particles to such a temperature, 1290°F-1470°F, that they solidify and do not cause difficulties due to sintering in the heat exchangers. The steam pressure in the boilers must be high enough to ensure that the wall temperature of the boiler tubes is above the dew point temperatures of the gases which contain SO_2 and SO_3. The dust in the boiler is easily removed by automatic soot-blowing equipment.

From the radiation boiler the gases are led at a temperature of 1290°F-1470°F to the heat exchanger. The heat exchanger preheats the air needed for smelting to a sufficiently high temperature by using the available heat content of the waste gases. The heat exchanger type used by Outokumpu Oy consists of groups of finned tubes cast from heat-resisting steel. The gases flow outside and the air inside the tubes. The dust is removed from the elements by


1
2
3
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11
12
13
14
AIR
SLAG
15
16
18
19
SLAG
17
Anode
Cu

1. CONCENTRATE STORAGE
2. BELT CONVEYOR
3. DRYER
4. DRYER COTTRELL
5. REDLERS
6. FEED HOPPER
7. CONCENTRATE BURNER
8. FLASH SMELTING FURNACE
9. WASTE HEAT RADIATION BOILER
10. HEAT EXCHANGER
11. PRIMARY AIR FAN
12. ELECTROSTATIC PRECIPITATOR
13. DAMPER FOR AUTOMATIC DRAFT CONTROL
14. GAS FANS
15. CONVERTER
16. ANODE FURNACE
17. CASTING WHEEL
18. SLAG CLEANING FURNACE
19. SLAG GRANULATING

SOURCE: Flash Smelting of Copper Concentrates, P. Byrk Et al.

Figure IV-3. Flowsheet of the Harjavalta Outokumpu Smelter

automatic soot-blowing equipment. Typically, the heat exchanger heats the air to about 930°F, and the waste gases are cooled to 660°F. The waste gases are then led to hot cottrells where most of the remaining dust is removed.

The flue dust collected from the waste heat boiler and ESP can be transported by a pneumatic elevator and then returned to the flash smelting furnace through a separate feed hopper.

From the ESP, the gases move through the exhaust gas fans which transport them to the sulfuric acid plant. These fans operate with an automatic draft control system so that the flash smelting furnace operates under a very small draft.

From the settler of the flash smelting furnace, the molten copper matte is tapped and transported in ladles to converters.

At Harjavalta, the converter department consists of three 11-1/2 ft x 21-1/2 ft converters. Since the matte grade is high (about 60% copper), only one converter at a time is necessary for blowing the flash smelter matte. All the smelter reverts and considerable amounts of scrap are smelted in the converter. Due to the high matte grade and the short blowing time, it is necessary to keep the converter hot between charges. This is accomplished by adding coke while waiting for the next charge; except for this, the converter operation is conventional.

Because of the high grade of matte, the copper content of the flash smelter slag is quite high. It is necessary to recover copper from this slag. This can be done in an oil-fired or an electric furnace, or by flotation techniques. (These are discussed in Section G "Metal Recovery from Slags.")

Blister copper is transferred to an oil-fired rotating anode furnace, fire-refined and cast into anodes.

2. Current Status of Flash Smelting

Since the establishment of the first flash smelter by Outokumpu at Harjavalta in 1949, a number of smelters have been built worldwide or are under construction. The following is a list of installations in operation or under construction:

Japan: Furukawa Mining Company, Dowa Mining Company, Nippon Mining Company, Mitsui Mining Company, Sumitomo Mining Company, Hubo Kyodo Smelting Company

Rumania: State Enterprise

Turkey: Kardeniz Bakir Isletemeteri

India: Indian Copper Corporation, Hindustan Copper Corporation

Australia: Peko-Wallsend Ltd.

U.S.A.: Phelps Dodge Hidalgo

U.S.S.R.: Norilsk Mining Metallurgical Combine

3. Effluents from Flash Smelting

Figure IV-4 is a schematic flow diagram of copper smelting using the Outokumpu flash furnace. The sources of pollutants are shown in four categories: air, solid, water, and fugitive. Table IV-9 shows the magnitude of these streams and the major constituents.

a. Air

The concentration of SO_2 in flash smelter gas is high, containing up to 13% SO_2. Conventional reverberatory furnace gas, on the other hand, typically contains 1.5-2.0% SO_2. These high-strength gases are most suitable for the manufacture of sulfuric acid. The variable strength/variable volume SO_2 gas stream from the converters can be mixed with the steady stream of flash smelter gas to provide a stream high enough in SO_2 for acid manufacture.

Table IV-10 shows how the SO_2 emissions from the flash furnace and converter change with different matte grades. At high matte grades, a large amount of sulfur is eliminated in the flash furnace. This improves acid plant performance since the volume and strength of the input stream are more constant. The overall distribution of sulfur in the smelter is shown in Table IV-11. It can be seen that the total emission to the atmosphere is only 2.8% of the total sulfur in feed. This is considerably lower than the emissions from conventional smelting where sulfur recovery from reverbs cannot be practiced economically. Because the EPA has concluded that reverb gases could not be treated economically for sulfur removal or sulfur recovery (while the gases from the flash furnace can be so treated), the comparison of these new smelting processes with the base line is not for equivalent degrees of sulfur control. The base line case recovers only 50-70% sulfur, while the new technology recovers over 90% sulfur.

Table IV-12 shows the cost of manufacturing sulfuric acid based on the assumption that the flash smelter gas and the converter gases are combined to form a steady flow of 56,900 scfm containing 10% SO_2.

b. Solid Wastes

Both flash smelter slag and converter slag are presently milled and floated at the Harjavalta smelter. In this case, the same amount of solid waste is generated as in the base case, but it consists of finely ground tailings. In calculating pollution control cost, we assume that three pounds of fine wet particles (90% <300 mesh) per pound of copper are pumped by pipeline to lined tailing ponds. In order not to tie up capital in a large pond, a new dike can be built every year in order to create a new settling basin of 475 ft in area by 24 ft in depth. The basins stay water covered until ready for final covering by three ft of dirt. The corresponding cost was estimated at \$190,000/yr, or \$1.90/ton of copper produced. The alternative approach is to use an electric furnace for slag cleaning. These two techniques are discussed separately in Section G.

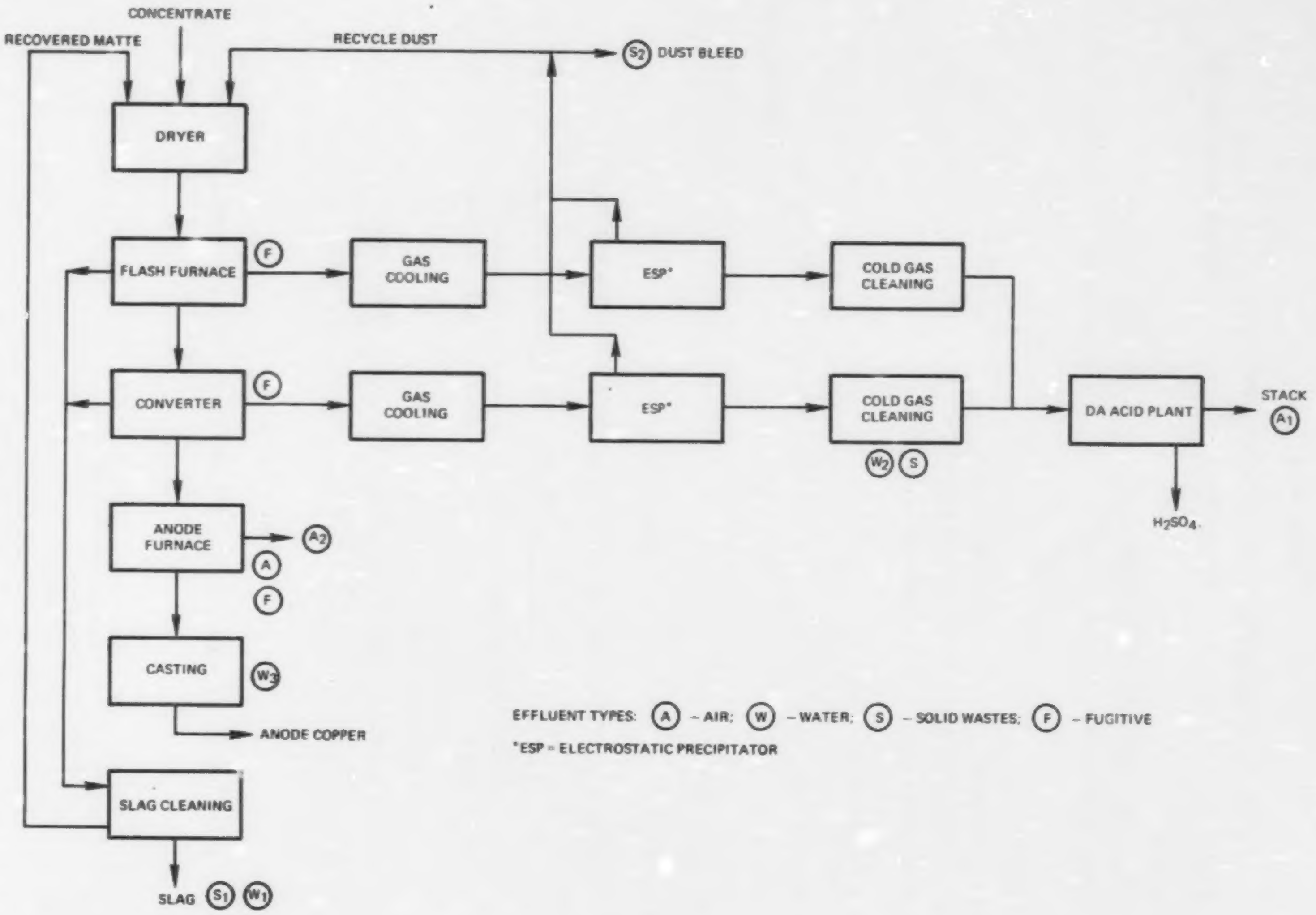

RECOVERED MATTE
CONCENTRATE
RECYCLE DUST
S_2 DUST BLEED
DRYER
FLASH FURNACE
F
GAS COOLING
ESP*
COLD GAS CLEANING
CONVERTER
F
GAS COOLING
ESP*
COLD GAS CLEANING
W_2 S
DA ACID PLANT
STACK
A_1
H_2SO_4
ANODE FURNACE
A_2
A
F
CASTING
W_3
ANODE COPPER
SLAG CLEANING
SLAG S_1 W_1
EFFLUENT TYPES: A – AIR; W – WATER; S – SOLID WASTES; F – FUGITIVE
*ESP = ELECTROSTATIC PRECIPITATOR

Figure IV-4. Sources of Emissions in the Outokumpu Flash Smelting Process

TABLE IV-9

EMISSIONS FROM OUTOKUMPU SMELTING

Stream	Stream Size	Major Constituents
• Air Pollution		
A-1 - Acid Plant Tail Gas	55,000 scfm	SO_2 - 0.05%
A-2 - Anode Furnace Gas	NA*	Flue Gas, Some SO_2
• Water Pollution		
W-1 - Slag Milling	1200 gal/ton	TDS, TSS
W-2 - Acid Plant Blowdown	720 gal/ton	TDS, TSS, Acidity
W-3 - Contact Cooling	180 gal/ton	TDS, TSS
• Solid Wastes		
S-1 - Cleaned Slag	3 ton/ton Cu	Iron Silicates
S-2 - Dust Bleed	0.3 ton/ton Cu	Copper Oxides, Minor Elements

*NA = Not Available

TABLE IV-10

SULFUR DISTRIBUTION IN FLASH FURNACE AND CONVERTER GASES

	Sulfur Distribution (%)			
Mattè Grade (%)	45	55	65	75
Feed	100	100	100	100
Furnace Gas	55	65	72	76
Converter Gas	45	35	28	24

Source: "New Developments in Flash Smelting," S.U. Harkki and J.T. Juusela, The Metallurgical Society of AIME, New York, 1974.

TABLE IV-11

SULFUR LOSS IN VARIOUS PROCESSING STEPS IN FLASH SMELTING

Step	% Loss
Drying	0.7
Smelting	1.0
Converting	1.0
Anode Furnace	0.1
Subtotal, Atmospheric Emissions	2.8
Slag Losses	1.2
Total Loss	4.0

Source: "New Developments in Flash Smelting", S.U. Harkki and J.T. Juusela, The Metallurgical Society of AIME, New York, 1974.

TABLE IV-12

OPERATING COSTS FOR AN ACID PLANT: OUTOKUMPU SMELTING

Outokumpu: 56,900 scfm
10% SO_2 Concentration
1094 ton/day of Acid
330 Operating Days/Yr
100,000 Tons of Anodes/Yr

Capital Investment (CI):	$\$10^6$
Waste heat boiler	2.26
Electrostatic precipitator & cold gas cleaning	1.12
DA acid plant	13.65
Total	17.03

Expected $H_2 SO_4$ Production Cost:	$/Yr	$/Yr
Variable Costs		
Direct Operating & Maintenance Labor 14 men @ $5.75/hr, 48 hr/week (L)	202,860	
Supervision @ 15% of Labor (S)	30,429	
Overhead @ 35% of Labor & Supervision	81,651	
Total Labor		314,940
Operating & Main. Supplies @ 2.4% of Cap. Cost	408,720	
Misc. Supplies	32,000	
Total Supplies		440,720
Energy - Fuel oil 5,000 bbl @ $11.60/bbl	58,000	
Electricity 180 kWh @ $0.021/kWh	1,364,655	
Total Energy		1,422,658
Other expenses - shutdown		280,000
Total Variable Costs		1,702,655
Fixed Costs		
Plant Overhead @ 65% (L + S)		151,638
Local Taxes & Insurace @ 2% of CI		340,600
Depreciation 14 years, straight line		1,216,428
Total Fixed Costs		1,708,666
Total Variable & Fixed Costs		3,411,321
ROI 20% of CI		3,406,000
Total charge against H_2SO_4 Manufacture		6,817,321
Total Charge/Ton of Acid		$18.88

Flue dusts are generated in amounts comparable to those mentioned for the base line (3 to 6% of the total weight of solids entering the smelter). Dusts are normally recirculated to the smelter, but again part of the dust stream may be diverted to avoid impurity build-up. The cost of disposing of dusts is the same as for the baseline: $24/ton of dust.

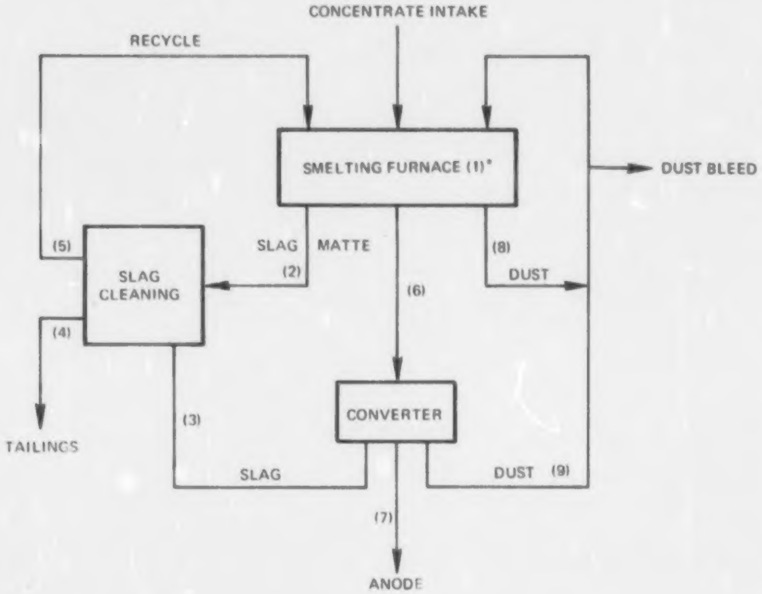
A schematic illustration of the flows of minor elements in a copper smelter using flash smelting reactors is shown in Figure IV-5. When making matte containing 60% copper, Table IV-13 gives a semi-quantitative idea of the distribution of the impurities among various streams.

c. Water

The water effluent streams from Outokumpu smelting are associated with the acid plant, the anode cooling, and the slag flotation (or granulation).

The aqueous effluents from the acid plant are similar in nature to those of the conventional smelter, but their volume is somewhat larger. The same control technology (lime and settle) can be applied at a cost of about $1.78/ton of copper produced. These costs are part of the costs shown in Table IV-16 for the acid plant.

The anode cooling stage is identical to the one implemented in conventional smelters.



*See Table IV-13 for explanation of ( ).

Figure IV-5. Diagram of Impurity Flow within a Smelter Using Outokumpu Flash Furnaces

TABLE IV-13

ESTIMATED DISTRIBUTION OF MINOR ELEMENTS AMONG THE VARIOUS STREAMS IDENTIFIED IN FIGURE IV-5
(Basis: Flash Furnace Impurities Input = 100)

	Flash Furnace			Converter					
STREAM #	Slag (2)	Matte (6)	Dust (8)	Slag (3)	Blister (7)	Dust (9)	Total Slag	Tailings to Pond (4)	Total Dust
Bi	2	18	80	0.2	0.7	17	2.2	Traces	97
As	10	20	70	2	3	15	12	4	85
Sb	30	50	20	11	13	75	41	29	45
Pb	10	10	80	2	Traces	9	12	10	89
Zn	30	10	60	3	Traces	7	33	29	67

Note: The solids discharged to the environment include the tailings and a fraction of the dust.

The water from the flotation tailings pond is returned to the flotation circuit. Some fresh water has to be added in order to compensate for the losses by evaporation, etc.

4. Technical Considerations

(1) Impurities

U.S. smelters treat a variety of materials which are characterized by their copper, iron, sulfur, and impurity content. The copper-bearing feed to smelters includes: 1) concentrates, 2) precipitates, 3) scrap, 4) ashes, 5) lead plant byproducts. When the feed to a smelter contains certain impurities such as arsenic, antimony, bismuth, lead, etc., in significant quantities, the feed is characterized as "dirty." In the United States, Asarco's El Paso, Texas and Tacoma, Washington smelters and the Anaconda smelter in Montana handle dirty concentrates (in levels above those routinely handled in Outokumpu flash smelting units in other countries).

To handle these impurities successfully, not only must they be removed from the product copper but they must also be split into two streams, an arsenic-rich stream and a lead/antimony-rich stream, so that these streams can be treated separately for byproduct recovery. The arsenic-containing stream is usually roasted in the copper smelter to produce arsenic trioxide and recover the copper in the dust while the latter stream is usually sent to a lead smelter for the recovery of lead, zinc, bismuth and antimony. Any arsenic in this latter stream is not recovered at the lead smelter but is returned to the copper smelter as a copper arsenide or "speiss" for further recovery of arsenic via roasting. To the best of our knowledge, the recovery of impurities from a mixed stream has not been practiced industrially.

Our discussions with Outokumpu indicate:

- High-impurity charges (6-8% As, 1-2% Sb) have not been treated in the flash furnaces. If such concentrates were charged, the flue dust from such an operation would be a mixture of Pb, As, and Sb compounds which could not be treated conventionally and which could present environmental difficulties.
- Outokumpu recommends roasting of the high arsenic materials in multiple hearth roasters for arsenic removal and the charging of calcines to the flash furnace. While this had been done successfully in a large-scale test, it has not been practiced routinely at any smelter.

(2) Scrap and Non-Sulfide Copper-Containing Materials

For the smelting of clean concentrates, the Outokumpu flash smelting process is capable of producing quality blister (over 99% copper). Flash smelting results in the production of high-grade matte. The capacity for smelting non-sulfide materials such as precipitate copper and scrap in the converter is reduced, since heat release in converting is less. However, with modifications in operating practice, such as oxygen enrichment of converter air and coke additions to the converter, scrap melting rates equivalent to conventional smelting are possible.

(3) One-Step Processing

The flash furnace also can be operated to produce copper (sulfur-saturated or oxygen-saturated) in one step by controlling the rate of oxidation in the furnace (Harkki and Juusela 1974). This approach is applicable only to clean concentrates; otherwise, impurities such as bismuth are concentrated in the metallic copper.

(4) Elemental Sulfur from Flash Furnace Off-Gas

As noted, the flash smelting furnace gas is high in sulfur dioxide and low in oxygen. The SO_2 can be reduced to elemental sulfur with pulverized coal and liquid or gaseous hydrocarbons at high temperature in the vertical uptake shaft, where the main part of the reduction is carried out. Since elemental sulfur is cheaper and safer to store and to transport than sulfuric acid, this process might be applicable when the smelter is distant from sulfuric acid markets.

The main problem in SO_2 reduction has been attaining a sufficiently rapid reaction rate to reach complete conversion of sulfur dioxide at the short retention times (2 to 4 seconds) required when handling large gas volumes. The reaction rate can be increased either by catalytic action or by raising the gas temperature. The latter approach is used in the Outokumpu process. Normally the temperature of the exit gas is sufficiently high, but it can also be raised by burning oil at the uptake of the settler. A thorough mixing of the reductant and process gas is necessary, and the choice of reductant also affects the reaction temperature.

The elemental sulfur process requires a flash furnace of slightly different shape and geometry. The gas-handling system comprises the following stages: A waste heat boiler cools the gases to 660°F. Particulates are removed in an electrostatic precipitator. The gases are then subjected to two stages of catalytic conversion to increase the yield of sulfur. The gases are reheated to 790°F before entering the first catalytic stage, where CO, COS, CS_2, and H_2, if any, are reacted. The gases are then cooled to 340°F in a boiler to reduce the temperature and condense elemental sulfur. The gases are then reheated to 465°F for the conversion of SO_2 and H_2S in the cold catalyzer. Afterwards, the sulfur is recovered in a scrubber and a demister. The recovery of purified sulfur from the flash furnace gases is about 90%.

By producing sulfuric acid from the converter gases and elemental sulfur from the flash smelter gases, the total recovery of sulfur in the copper smelter exceeds 90%.

This elemental sulfur process is being used only in two locations on copper concentrates: In Botswana, Africa on copper-nickel concentrates using coal as the reductant, and at Phelps Dodge's Hidalgo smelter (under construction) using light naphtha as a reductant. (Outokumpu's Pori plant operates on a feed of pyrites using a naphtha reductant.)

5. Economic Factors

a. Capital and Operating Costs

Table IV-14 shows estimates of capital and operating costs (including pollution control) based on data presented by Schwartz (1975) and by Outokumpu. The capital costs are about the same as for roast-reverb smelting. The following basis has been used:

- Costs include pollution control and credit for acid sales.
- Oxygen enrichment is not utilized. This case was selected to serve as a basis for the subsequent evaluation of oxygen enrichment in Section F. Oxygen enrichment is preferred in many locations with existing flash smelters, since the capacity of a unit can be increased up to 50% with oxygen with a consequent decrease in fuel costs and fixed charges per unit of output.
- The calculations procedure is consistent with the calculation for the base case.

TABLE IV-14

OPERATING COSTS: OUTOKUMPU FLASH SMELTING
(Basis: Copper sulfide concentrates, 28.6% Cu, 29.3% Fe, 33.4% S
100,000 S ton/yr of anode copper)

	Unit	$/Unit	Units/Ton	$/Ton CU
CAPITAL INVESTMENT (CI) $/annual ton			$750	
OPERATING COSTS				
VARIABLE COSTS				
Silica Flux	ton	8.00	0.86	6.88
Limestone	ton	10.00	---	---
H_2SO_4 credit	ton	10.00	3.33	(33.30)
Oxygen	ton	15.00	---	---
Fuel Oil	10^6 Btu	2.00	12.7	25.40
Natural Gas	10^6 Btu	0.65	1.3	0.85
Electricity	kWh	0.021	366.40	7.69
Water: Process	10^3 gal	0.02	1.06	0.21
Cooling	10^3 gal	0.05	2.00	0.10
Refractories	ton	300.00	0.014	4.20
Direct Operating and Maintenance Labor (L)	Man-hr	5.75	6.2	35.65
Supervision (S)	L	15% L	---	5.35
Maintenance Materials	CI	4% CI	---	30.00
Labor Overhead	L+S	35% (L+S)	---	14.35
TOTAL VARIABLE COSTS				97.38
FIXED COSTS				
Plant Overhead	L+S	65% (L+S)	---	26.65
Local Taxes & Insurance	CI	2% CI	---	15.00
Depreciation	CI	7% CI	---	52.50
Capital Recovery	CI	20% CI	---	150.00
TOTAL FIXED COSTS				244.15
TOTAL COSTS				341.53

b. Comparison with the Base Line

(1) Energy Use

Table IV-15 shows that energy use is decreased compared to a roast-reverb smelter. Fuel oil consumption decreases from 18.6 to 12.7 10^6 Btu/ton copper, electricity consumption decreases from 440 to 370 kWh/ton copper. This is because the heat of oxidation of sulfur and iron is used to melt the charge and energy is recovered from all high temperature waste heat streams. Since both technologies can use any fossil fuel in the smelting unit, there is no further conservation of energy of a different form.

The energy data discussed above are those estimated by us on a basis comparable to the base case. Outokumpu has published energy consumption data based on their operating experience at the Harjavalta smelter (Juusela 1974). Because the Harjavalta smelter uses oxygen enrichment, the results are not directly comparable. Also the power requirements for the acid plant are not included. We present Outokumpu's data without any alterations for interested readers in Table IV-15.

(2) Pollution Aspects

The flash smelter and its associated acid plant recover a higher amount of SO_2 (95%) compared to roast-reverb smelting (70%). Table IV-16 shows the pollution control costs for the process. Comparison of this table with Table IV-7 shows that because the Outokumpu process produces a much more concentrated SO_2 stream, the pollution control costs per ton of copper are comparable in spite of the higher degree of sulfur recovery.

For all smelting processes, the transfer of matte to the converter and converter operations are a major source of fugitive emissions.

(3) Byproducts

When acid markets exist near a smelter, the conversion of the SO_2-containing streams to sulfuric acid is the most cost-effective way of preventing their emission to the atmosphere. However, a market for acid is not always assured, particularly because of the wide swings in price of elemental sulfur with time and the availability (in the future) of increasing quantities of byproduct sulfur from crude oil desulfurization. Alternative ways of disposal are neutralization with limestone which may cost 1-2¢/lb copper or sulfur and the conversion of SO_2 to elemental sulfur (for storage, if markets are unavailable), which may cost more than 4¢/lb copper or sulfur.

(4) Cost Comparison

Comparison of Tables IV-6 and IV-14 indicates that the cost of flash smelting is slightly lower, primarily because it is more energy efficient. The energy costs for roast-reverb smelting are about $44/ton of copper vs $28 for flash smelting. The total operating costs for both examples are about 17¢/lb. Even if acid credits are ignored, the process is still somewhat cheaper in new facilities based on clean concentrates.

TABLE IV-15

ENERGY BALANCE FOR OUTOKUMPU FLASH SMELTING

BASIS: 1000 Metric ton/day Wet Concentrate (25% Cu, 8% H_2O)
Transformed to Anode Copper.

Process Step	Requirements by Energy Form/Ton of Charge Steam (kg)	O_2 (NM^3)	Electricity (kWh)	Oil (kg)
Drying	110	-	4	8
Flash Smelting		100	15	15
Slag Flotation			50	
Converting		10	15	
Anode Casting			2	6
Superheating of Steam (70 atm)				9
Sub-Total	110	110	86	38
Energy Equivalents			(3)	22
Heat Recovered As Steam	900			
Less Process Steam Used	110	(2)		
Less Steam Used For Oxygen Plant	230			
Surplus Steam	560		(4)	-34
NET ENERGY REQUIRED (kg oil)				26
(10^6 Btu)				1
If Acid Plant is Included				
NET ENERGY REQUIRED (kg oil)				58
(10^6 Btu)				2.2

NOTES:

1. Excludes acid production. For single contact plants, power requirements are equivalent to about 125 kWh/ton of feed.
2. Oxygen to steam equivalence based on actual operating data.
3. Electricity to oil equivalence based on standard power plant efficiency of 10,500 Btu/kWh.
4. Steam to oil equivalence based on standard boiler efficiency.
5. Original table in metric units; not converted to English units.

Source: Outokumpu, private communications

TABLE IV-16

COST OF POLLUTION CONTROL IN THE OUTOKUMPU FLASH SMELTING PROCESS

	Units	$/Unit	Units/Ton	$/Ton of Copper
Acid Manufacture	Ton Acid	18.88	3.33	62.87
Credit for Acid Sales	Ton Acid	(10.00)	3.33	(33.30)
Slag Disposal (Granulation)	Ton Slag	5.00	3	15.00
Water Pollution Control	Ton	-	-	3.25
Dust Disposal	Ton Dust	24.00	0.02	0.48
Total Pollution Cost				48.30

Source: Arthur D. Little, Inc. estimates.

D. THE NORANDA PROCESS

1. Concept and Operation

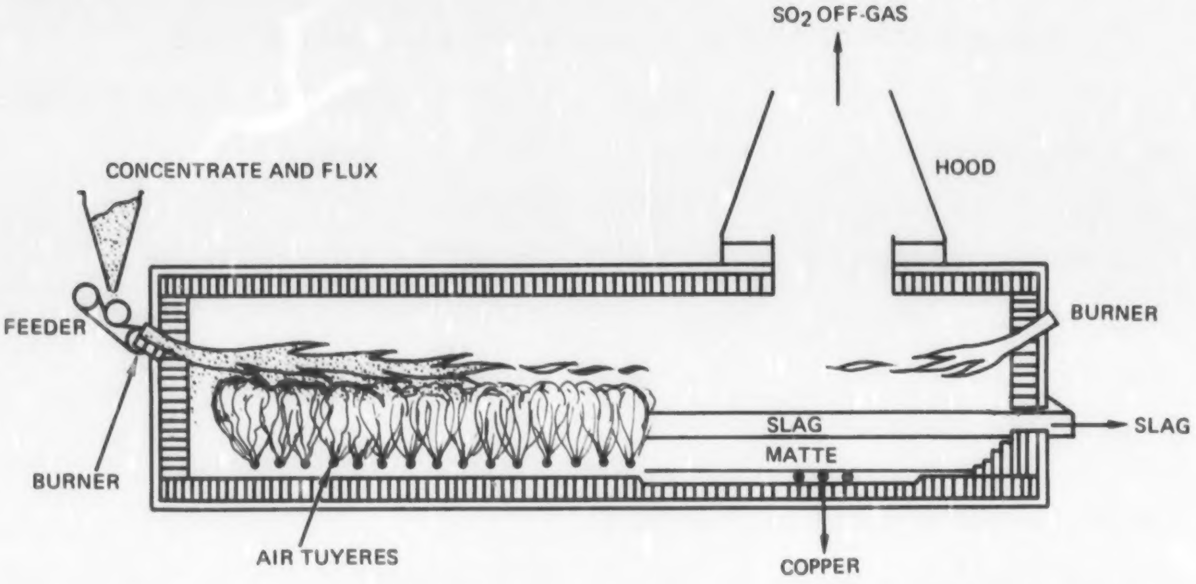
a. Introduction

The Noranda process combines in a single reactor the three operations of roasting, smelting, and converting of copper concentrates. The heat losses suffered during the transfer of concentrate from the roaster to the reverberatory furnace are suppressed, as well as the heat losses occurring during the transfer of the matte from the reverberatory furnace to the converter. In addition, the net heat of oxidation is used for smelting. Liquid copper, matte, and slag coexist in three layers resting on top of each other. Air is blown into the bath through tuyeres, and oxygen enrichment to 35-40% tends to make the process autogenous, so that extraneous fuel can be kept at a minimum during the blow. A continuous flow of high strength (over 10% SO_2) sulfur dioxide gas is generated, which is suitable for the manufacture of sulfuric acid.

b. Description of the Reactor and Plant Layout

The following description and figures are largely abstracted from various papers published by Noranda's staff members. Figure IV-6 shows a schematic drawing of the Noranda process reactor. A flowsheet of the process appears as Figure IV-7.

The reactor is a horizontal, cylindrical furnace with a series of tuyeres located along the reactor in the smelting and converting zone. The reactor can be rotated to bring the tuyeres out of the bath when a stoppage in the process is needed for maintenance or because of loss of converting air pressure.


SO$_2$ OFF-GAS
CONCENTRATE AND FLUX
HOOD
FEEDER
BURNER
SLAG
SLAG
MATTE
BURNER
AIR TUYERES
COPPER

SOURCE: Weddick, 1974.

Figure IV-6. Schematic of the Noranda Process Reactor

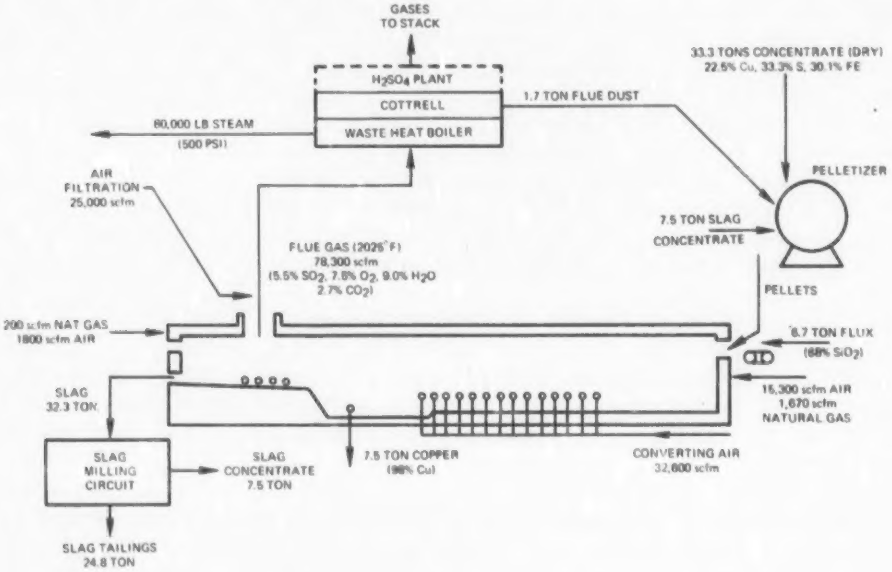

GASES
TO STACK
H$_2$SO$_4$ PLANT
COTTRELL
WASTE HEAT BOILER
80,000 LB STEAM
(500 PSI)
1.7 TON FLUE DUST
33.3 TONS CONCENTRATE (DRY)
22.5% Cu, 33.3% S, 30.1% FE
PELLETIZER
AIR
FILTRATION
25,000 scfm
7.5 TON SLAG
CONCENTRATE
FLUE GAS (2025°F)
78,300 scfm
(5.5% SO$_2$, 7.8% O$_2$, 9.0% H$_2$O
2.7% CO$_2$)
PELLETS
200 scfm NAT GAS
1800 scfm AIR
8.7 TON FLUX
(68% SiO$_2$)
SLAG
32.3 TON
15,300 scfm AIR
1,670 scfm
NATURAL GAS
SLAG
MILLING
CIRCUIT
SLAG
CONCENTRATE
7.5 TON
7.5 TON COPPER
(98% Cu)
CONVERTING AIR
32,800 scfm
SLAG TAILINGS
24.8 TON

Figure IV-7. Material Flowsheet (per hour) for Noranda Process Plant (800 ton concentrate/day)

An opening in the roof of the reactor, away from the tuyere zone, allows off-gases to escape into a hood, spray chamber, or waste heat boiler and electrostatic precipitator. The cleaned gases are then converted to sulfuric acid. Other design features are burners at each end of the furnace, a feed port for charging copper concentrate, flux, and slag concentrate by means of a belt slinger, and separate tapholes for tapping slag and copper.

The reactor bath consists of layers of slag, high-grade matte, and metallic copper. Copper concentrate, silica flux and concentrate recovered from slag milling are charged on the surface of the bath in the smelting and converting zone, which is strongly agitated by air or oxygen-enriched air injected through the tuyeres.

Under the dynamic conditions existing in the bath, copper is produced even though the bath contains more iron than an equilibrium system. The copper produced by oxidation settles by gravity to the bottom of the vessel, and the flux combines with oxidized iron to form a slag which floats on a large volume of matte. This volume is normally kept constant by blowing air or oxygen-enriched air through the tuyeres at a rate proportional to the rate of copper concentrate addition so that all the input sulfur and iron is oxidized to produce copper and slag. At the same time, the rate of flux addition is controlled proportionally to the concentrate input rate to maintain an Fe/SiO_2 ratio in the slag of 1.6. The slag concentrate addition is also kept at a constant ratio to the copper concentrate. Copper and slag are tapped at regular intervals so as to maintain relatively constant levels of matte, slag and copper. These are the basic control parameters of the Noranda process.

By introducing the air at a sufficient depth below the surface of the matte, 95% or more of the oxygen reacts with the matte. This consistently high utilization of oxygen makes it possible to predict accurately the amount of oxygen required for each ton of concentrate of a particular composition. The intense mixing action of the air jets maintains the bath in turmoil and thus provides a high heat transfer rate from the copper sulfide matte, where heat is generated by the converting reactions, to the slag phase and to the concentrate charge on the surface of the bath.

The turbulence generated by air jets, and the fact that the slag is in contact with a high grade matte, causes the slag to contain 10-12% copper, most of which is present as entrained metal globules. The tapped slag is allowed to cool slowly over a period of days, crushed to 90% -324 mesh and subjected to flotation. A tailing containing 0.5% copper is obtained. The copper loss in the tailings is equivalent to the copper loss with a 0.35% copper slag produced in a reverberatory furnace. A slag concentrate containing 50% copper is also produced. It is mixed with flue dust in a pelletizing machine and recycled to the reactor.

The raw copper produced by the Noranda process contains 1.5 to 2% sulfur, which is somewhat higher than that contained in blister copper from the conventional smelting process. This copper is transferred to a converter until a charge of about 120 tons is collected. The sulfur is then oxidized by blowing air through the tuyeres for 10-15 minutes, followed by fire refining in a rotary anode furnace, and then casting into anodes for electrolytic refining.

When the concentrate feed contains impurities such as bismuth, it is preferable to produce a high grade matte in the Noranda reactor and convert the matte separately. Bismuth is volatalized and collected in the converter dust. Under these conditions, the copper content of the slag is lowered to 6-7%, but the reactor slag is still amenable to the same flotation treatment. The reactor matte is charged to conventional Pierce-Smith converters and is further processed as in the conventional process.

2. Current Status

This process was developed by Noranda Mines Ltd. during the sixties. A semi-industrial scale pilot plant with a rated capacity of 100 tons of concentrate per day has been in operation since May 1968, at the Noranda, Quebec smelter. Based on the results of the experimental installation, an 800 ton/day industrial plant was built in Noranda and went on stream in March 1973, using air for converting. Oxygen enrichment has since improved the productivity of this unit. It was shown that increasing the oxygen content of the air blown through the tuyeres from 21% to 35% more than doubled the instantaneous productivity of the reactor.

The reactor presently operated at Noranda, Quebec is now making high grade matte containing 70-72% copper. This practice has the following advantages:

- The refractories around the tuyeres last longer. The longest campaigns of copper-producing operations were of the order of 72 days, whereas the campaign of matte making was in its 105th day on October 29, 1975. It was expected to last at least another two weeks.
- The level of impurities in the final blister copper is much more favorable. This has far reaching implications concerning the energy consumption during refining and the quality of the cathodes themselves.
- A greater flexibility of the integrated operation may be achieved, as mattes of chosen grades can be made.

Kennecott Copper Corporation has planned the construction of a plant with a rated capacity of 250,000 ton/yr of blister copper. This plan includes three reactors of the same dimensions as the present Noranda unit (800 ton/day when making copper with nonenriched air).

Enough experience has been accumulated so that one may assess the main features of the process. A comparison of the highlights of the Noranda continuous smelting process as published by Noranda and conventional smelting appears in Table IV-17. Table IV-18 shows a material balance. These data have been used by us in our estimation of process costs.

3. Effluents

Figure IV-8 is a schematic flow diagram of copper smelting using Noranda reactors. The sources of pollutants are identified for four categories: air, solid, water, and fugitive. These streams are essentially similar to those described earlier. Table IV-19 shows the magnitude of these streams and the major constituents.

TABLE IV-17

COMPARISON OF THE NORANDA PROCESS VS. CONVENTIONAL REVERBERATORY-CONVERTOR WORKS

	Reverb.	Noranda (making matte)	Noranda (making copper)
Process Type	Batch Converting	Continuous Matte Making Batch converting	Continuous Reactor Copper Making
Capacity, metric tons concentrate/day	830	900-1800	720-1450
Converters	2	1	1
Internal furnace volume/m^3	1485	1200	
Matte grade	20-40	68-72	no matte produced
Sulfur content of blister(1)	0.01	0.01	0.01
Smelter slag, % Cu	0.3-0.6	0.5-0.6	10-12
Smelter slag milled	no	yes	yes
Power for milling slag, kWh/ton slag	0	26	26
Total copper in slag % Cu	0.3-0.6	0.3-0.6	0-0.3
Oxygen consumed, ton/ton conc.	0	0-0.3	0-0.3
Total fuel consumption, 10^6 Btu/ton	24	n.a.	min 12
Smelter gas, continuous % SO_2 conc.	1-2	10-12	10-12

NOTE: (1) The Noranda reactor copper contains 1.5-2% S. It has to be finally converted in a few minutes to 0.01% S. This operation can take place either in a converter or during an extended fine refining operation.

Source: Noranda Mines Ltd.

TABLE IV-18

TYPICAL COMMERCIAL OPERATION WITH AIR
(Tons)

Tuyere blowing rate, scfm	27,667	% oxygen in tuyere air	21.0
Fuel type	oil	% oxygen in combustion air	21.0
		oxygen, tons/day	0.0

MATERIALS BALANCE

	Throughput dry tons/ day	Composition %					
		Cu	Fe	S	SiO_2	Zn	H_2O
REACTOR INPUT							
Copper Concentrate	800.0	24.9	29.0	32.2	4.1	4.9	10.0
Slag Concentrate	182.3	50.0	17.4	5.6	10.9	1.5	12.0
Flux	169.7	0.0	4.4	0.9	68.7	0.0	7.0
Dust	32.0	20.0	10.0	12.0	0.0	19.3	0.0
REACTOR OUTPUT							
Copper	200.8	97.8	0.2	2.0	0.0	0.0	0.0
Slag	784.7	12.0	34.5	1.3	21.6	4.9	0.0
Dust	32.0	20.0	10.0	12.0	0.0	19.3	0.0
MILL INPUT							
Slag	784.7	12.0	34.5	1.3	21.6	4.9	0.0
MILL OUTPUT							
Slag Concentrate	182.3	50.0	17.4	5.6	10.9	1.5	12.0
Slag Tail	602.4	0.5	39.7	0.0	24.8	5.9	12.0

Copper Loss, % of copper in new metal bearing material: 1.51

HEAT BALANCE

	10^6 Btu/ ton conc.	Distribution %
HEAT INPUT		
Converting Reactions	3.56	67.8
Net Heat From Fuel	1.69	32.2
Total	5.25	100.0
HEAT OUTPUT		
Converting Gas (excluding combustion gas)	3.35	63.8
Heat Content of Copper	0.16	3.0
Heat Content of Slag	1.20	22.9
Heat Loss	0.54	10.3
Total	5.25	100.0

Total fuel required, million BTU/ton copper concentrate: 4.8

Useful steam from waste heat boiler: 101,420 pounds at 660°F and 600 PSIA

OFF GAS DATA

Off gas continuously available to acid plant (including 75% dilution). Dry scfm	94,631			
Moisture content (% wet basis)	6.6			
Composition (% dry basis)	N_2 81.5	O_2 9.8	SO_2 4.5	CO_2 4.2

Source: Noranda Mines, Ltd.

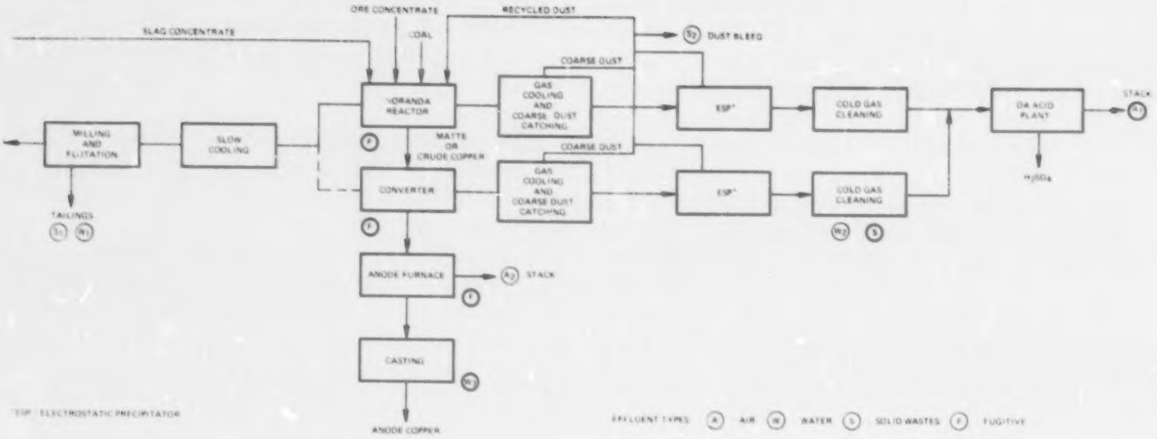

ORE CONCENTRATE
RECYCLED DUST
SLAG CONCENTRATE
COAL
S2 DUST BLEED
COARSE DUST
NORANDA REACTOR
GAS COOLING AND COARSE DUST CATCHING
ESP*
COLD GAS CLEANING
DA ACID PLANT
STACK A1
H2SO4
MILLING AND FLOTATION
SLOW COOLING
F
MATTE OR CRUDE COPPER
COARSE DUST
CONVERTER
GAS COOLING AND COARSE DUST CATCHING
ESP*
COLD GAS CLEANING
TAILINGS
S1 W1
F
W2 S
ANODE FURNACE
A2 STACK
F
CASTING
W3
*ESP - ELECTROSTATIC PRECIPITATOR
ANODE COPPER
EFFLUENT TYPES A AIR W WATER S SOLID WASTES F FUGITIVE

Figure IV-8. Sources of Emissions in the Noranda Process

TABLE IV-19

EMISSIONS FROM NORANDA SMELTING

Stream	Stream Size	Major Constituents
• Air Pollution		
A-1 - Acid Plant Tail Gas	55,000 scfm	SO_2 - 0.05%
A-2 - Anode Furnace Gas	NA*	Flue Gas, Some SO_2
• Water Pollution		
W-1 - Slag Milling	<1200 gal/ton	TDS, TSS
W-2 - Acid Plant Blowdown	720 gal/ton	TDS, TSS, Acidity
W-3 - Contact Cooling	180 gal/ton	TDS, TSS
• Solid Wastes		
S-1 - Cleaned Slag	3 ton/ton copper	Iron Silicates
S-2 - Dust Bleed	0.3 ton/ton copper	Copper Oxides, Minor Elements

*NA = Not Available

a. Air

Off-gases leave the reactor through a water-cooled hood. The coarse dust particles are collected in the cooling chamber connected to the hood, while fine particulates are collected in an electrostatic precipitator. Part of the dust is treated for minor elements elimination, while most of it is sent back to the pelletizer and recycled to the furnace.

The sulfur dioxide concentration in the reactor atmosphere is around 23% on a dry basis. Because of air infiltration around the hood, the gas stream entering the acid plant contains 10-13% SO_2. This stream is only interrupted 5% of the time during tapping, and can be mixed with the off-gases of other reactors and Pierce-Smith converters. Air in-leakage (thereby preventing atmospheric emissions) is high but does not affect the subsequent H_2SO_4 plant since its operation is at or below the 10-13% SO_2 concentration. This steady, high SO_2 gas generation level is a significant advantage over the conventional reverberatory process.

After dry gas cleaning, wet gas cleaning equipment is required to scrub out the remaining fine particulates. The gas can then be treated in a double contact acid plant. The total sulfur recovery is as high as the one achieved with the Outokumpu flash smelting process, and Tables IV-10 and IV-11 would apply to the Noranda process.

The fugitive emissions occur during matte transfer and converter operations and consist of SO_2 and particulate emissions.

b. Solid Wastes

Both converter slag and reactor slag need beneficiation, and this is presently done by milling and flotation. For each pound of copper, four pounds of slag containing an average 8% copper are treated; the products are three pounds of tailings (90% <300 mesh) and one pound of slag concentrate returned to the smelter's feed. These tailings require lined tailing ponds. As noted earlier, a new dike can be built every year in order to create a new basin of 475 sq ft in area by 24 ft of depth to accept the calculated volume of discharge. These basins stay water-logged until ready for final covering by three feet of dirt. Supernatant water is recovered and reused in the milling circuit. The corresponding cost for solid waste disposal was estimated at $190,000/yr, or $1.90/ton of copper produced.

Flue dusts are generated in amounts comparable to those mentioned for the base line (2 to 5% of the total weight of solids entering the smelter according to Noranda). Dusts are recirculated to the smelter, unless part of it must be diverted to avoid impurity build-up or to recover some of these impurities for commercial purposes. The cost of disposal of impure dust is estimated at $24/ton of dust.

The flow of minor elements in a copper smelter using the Noranda reactor is similar to that shown in Figure IV-5. But, when making matte containing 70% copper by the Noranda process, the distribution of the impurities among the various streams shown in Figure IV-5 is as shown in Table IV-20.

TABLE IV-20

NORANDA PROCESS - DISTRIBUTION OF MINOR ELEMENTS WHEN MAKING 70% GRADE MATTE

Basis: 100 units of each element entering the reactor

Stream #	Reactor Input (1)	Reactor Tapped Slag (2)	Tailings (4)	Volatilized in Reactor (6)	Staying in Matte (9)	Residual in Blister (5)
Pb	100	13	10	74	13	Traces
Zn	100	68	60	27	6	Traces
As	100	7	4	85	9	0.8
Sb	100	28	19	57	15	4.5
Bi	100	21	16	70	9	2.3

Remarks: (1) The environment receives the tailings (Stream #4) and the portion of the dusts that is not recycled, i.e., usually 10-20% of the total dust discharge.

(2) The impurities remaining in the matte are largely volatilized in the converter and collected as converter dust and in acid plant blowdown.

Source: Noranda Mines, Ltd., and Arthur D. Little, Inc. estimates

A detailed discussion of the impurity distribution in the Noranda process appears in the section "technological factors" because impurities have major impact on the quality and mechanical properties of the product copper.

c. Water Pollution

The water streams in Noranda smelters are those associated with the acid plant scrubbers, anode cooling, and the slag milling and flotation circuit.

The combined off-gases go through a wet cleaning stage before entering the acid plant. The nature of the aqueous effluents generated is the same as for the base case or for Outokumpu smelting. Costs and dimensions given for the Outokumpu flash smelting process are identical to those for the Noranda process.

Anode cooling waters are also identical to those generated in conventional smelters.

The water from the slag milling circuit flows with the tailings to the lined settling ponds. The water is recycled to the milling circuit. The flotation agents are mainly absorbed on the concentrates and subsequently pyrolyzed in the smelting furnace.

4. Technical Considerations

a. Impurities

A number of minor elements are usually present in the feed to the smelter. Their overall elimination and possibility of recovery are governed by thermodynamic, kinetic and process parameters. Depending on the prevailing oxygen and sulfur potential, they may be present as sulfides, oxides, or dissolved metals.

During the smelting process, elimination takes place by two mechanisms, slagging and volatilization. Those impurities not eliminated by these mechanisms remain in the anodes and affect the operation of the electrolytic refinery. Elements such as lead, bismuth, arsenic, and antimony are difficult to remove by oxidation and separation into an oxide slag phase. However, they can be volatilized during smelting. Lead, bismuth, and tin have high vapor pressures both as sulfides and as oxides, but are best removed under reducing conditions. Arsenic, tin and antimony may be removed only as oxides or sub-oxides. Arsenic, antimony, and bismuth are more soluble in copper than in matte. Thus, their presence in significant amounts means that the Noranda reactor has to be operated for making matte.

When making copper, the Noranda process combines a high oxygen potential and the presence of metallic copper, causing elements such as Pb, Bi and Sb to stay with the copper. These elements are not considered desirable in anodes used for conventional electrorefining because in some cases they decrease the hydrogen overvoltage and the cathodes evolve hydrogen instead of depositing copper, with a corresponding increase in energy consumption. In other cases, these impurities may transfer to the cathode, with detrimental effects on the electrical and mechanical properties of the copper produced. Since conventional electrorefining does not remove these materials very effectively, this is an open area for research. For example, the synergistic effect of the combined presence of bismuth, arsenic, and antimony in the anodes is not well explored. These impurities might be rejected more effectively as anode mud under some circumstances. Selenium and tellurium belong to the same chemical group as sulfur and they tend to stay in the matte phase. Their transfer to the copper phase is, therefore, lower than in conventional blister copper since the matte is never tapped in making copper in the one-step process.

Cobalt, tin, nickel, zinc, and lead are easily oxidized in the slag. The solubility of silver and copper in the slag is also favored by the high oxygen potential that prevails when making copper. The reactor slag is presently treated by milling and flotation at the Noranda smelter. Table IV-21 shows the recovery of minor elements in slag concentrate by this process. Should it be economically desirable to recover such valuable elements as lead, zinc, nickel, cobalt, or other easily oxidizable elements, a pyrometallurgical slag treatment could be adopted. Typically an electric arc furnace provides a suitable reducing environment and pyrite additions can provide the stoichiometric amount of sulfur to recover dissolved metallics as sulfides from the slag to a matte phase.

TABLE IV-21

RECOVERY OF MINOR ELEMENTS IN SLAG MILLING

Element	Percent Recovery In Slag Concentrate
Cu	97
S	86
Fe	11
Pb	16
Zn	13
Cd	22
As	35
Sb	29
Bi	23
Se	73
Te	58
Ni	11
Sn	17
Au	95
Ag	93

Source: Mackey 1975

Lead and zinc are the largest contributors to the overall dust generation. The dusts also contain significant amounts of the other elements, as noted earlier. Bismuth, selenium, and tellurium volatilization is mainly achieved by the flushing action of the tuyere gas. Arsenic and antimony would appear to be volatilized during the early stage of concentrate smelting. Table IV-22 shows the observed distribution of the minor elements among the off-gases, the slag, and the reactor copper. One way to avoid building up the amount of impurities in the system is to treat part of the dust before recycling it to the reactor. The amount of dust treated depends on the amount of impurities fed with the reactor charge and also on the overall acceptable level from the viewpoint of the quality of the final product. As usual, two separate treatment circuits will recover arsenic in one stream and lead, arsenic, bismuth, and antimony in the other stream.

Fire refining of reactor copper is a further opportunity to reduce the concentration of As, Sb, and Bi in the copper. This behavior of impurities (particularly Bi, Sb, and Pb) means that under conditions of high oxygen potential the Noranda process cannot be applied to a concentrate containing these impurities until electrorefining practice is improved for removal of these impurities. This is the main reason why the initial applications of the Noranda process focus on matte making and the elimination of the impurities via volatilization in the batch converter operation. After converting the matte, the concentrations obtained in the anode copper are similar to those resulting from conventional copper smelting.

TABLE IV-22

OBSERVED DISTRIBUTION OF MINOR ELEMENTS IN NORANDA PROCESS MAKING COPPER[1] (30% Oxygen Enriched Air)

Element	Percent Distribution in Reactor Streams[2]		
	Off-gas(Dust) (D_1)	Tapped Slag (D_2)	Reactor Copper (D_3)
Pb	21	77	2
Zn	14	86	0.2
Cd	95	4.5	0.5
As	39	14	47
Sb	18	52	30
Bi	43	42	15
Se	60	21	19

[1] Test Conditions
Copper concentrate analysis: 24.6% Cu, 28.8% Fe, 32.5% S
Fe/SiO_2 ratio in slag: 1.5

[2] $D_1 = \frac{\text{tons of X in off-gas (dust)}}{\text{tons of X in reactor feed}}$

$D_2 = \frac{\text{tons of X in tapped slag}}{\text{tons of X in reactor feed}}$

$D_3 = \frac{\text{tons of X in reactor copper}}{\text{tons of X in reactor feed}}$

Source: Mackey 1975

b. Scrap

The Noranda process has the same limitations on scrap reuse as the Outokumpu flash smelting process. In the matte version of the process, only a limited amount of bulky scrap can be melted in the converters.

There is no thermal limitation on melting scrap in the Noranda reactor since excess heat, if needed, can be supplied via external extraneous fuel or increased oxygen enrichment. The limitation would be in terms of the particle size of scrap and reverts which can be fed to the reactor.

c. The Use of Oxygen

The use of oxygen enrichment in the Noranda process increases unit capacity, decreases capital investment per unit of output, and improves energy efficiency. Pertinent data published by Noranda are presented in Table IV-23 and Figures IV-9 and IV-10.

5. Economic Factors

a. Capital and Operating Costs

Modern smelters installed in the United States should be expected to cost about $750 per annual ton of anode copper (rated capacity) for the major new

TABLE IV-23

TYPICAL COMMERCIAL OPERATION WITH OXYGEN
(Tons)

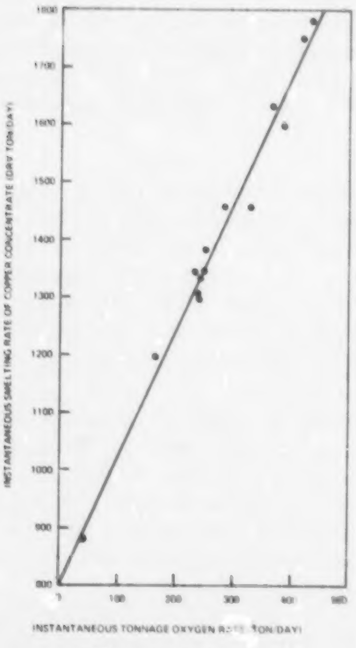
Tuyere blowing rate, scfm Fuel type	33,700 oil	% oxygen in tuyere air % oxygen in combustion air oxygen, tons/day	26.0 50.0 421.[illegible]

MATERIALS BALANCE							
	Throughput dry tons/day	Composition %					
		Cu	Fe	S	SiO_2	Zn	H_2O
REACTOR INPUT							
Copper Concentrate	1000.0	25.9	29.0	32.2	4.1	4.0	10.0
Slag Concentrate	384.5	50.0	17.4	5.6	10.9	1.5	12.0
Flux	335.4	0.0	4.4	0.9	68.7	0.0	7.0
Dust	64.0	20.0	10.0	12.0	0.0	10.3	0.0
REACTOR OUTPUT							
Copper	401.5	97.[illegible]	0.2	2.0	0.0	0.0	0.0
Slag	1389.3	12.0	34.5	1.3	21.6	5.1	0.0
Dust	64.0	20.0	10.0	12.0	0.0	10.3	0.0
MILL INPUT							
Slag	1389.3	12.0	34.5	1.3	21.6	5.1	0.0
MILL OUTPUT							
Slag Concentrate	384.5	50.0	17.4	5.6	10.9	1.5	12.0
Slag Tail	1204.8	0.5	38.7	0.0	24.8	6.1	12.0
Copper Loss, % of copper in new metal bearing material 1.51							

HEAT BALANCE		
	Million BTU/ton conc	% Distribution
HEAT INPUT		
Converting Reactions	3.56	89.9
Net Heat From Fuel	0.40	10.1
Total	3.96	100.0
HEAT OUTPUT		
Converting Gas (including combustion gas)	2.33	58.8
Heat Content of Copper	0.16	4.0
Heat Content of Slag	1.20	30.3
Heat Loss	0.27	6.8
Total	3.96	100.0
Total fuel required, million BTU/ton copper concentrate 0.62 Useful steam from waste heat boiler 75,300 pounds at 600°F and 600 PSIA		

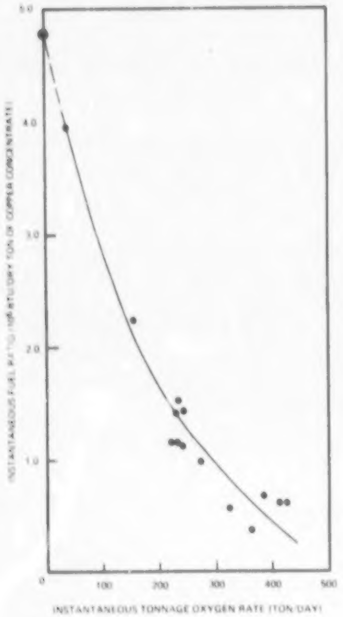
OFF GAS DATA				
Off gas continuously available to acid plant (including 75% dilution) Dry SCFM	63,516			
Moisture content (% wet basis)	11.4			
Composition (% dry basis)	N_2 74.5	O_2 10.7	SO_2 13.2	CO_2 1.6

Source: Noranda Mines, Ltd.



SOURCE Noranda Mines, Ltd.

Figure IV-9. Smelting Rate Versus Tonnage Oxygen Added



SOURCE: Noranda Mines, Ltd.

Fig. IV-10

Figure IV-10. Fuel Ratio Versus Tonnage Oxygen Added

pyrometallurgical processes considered here. We have used this figure since no company has yet built a complete smelter using Noranda reactors. Capital costs published by Kennecott (Matheson, 1974 and Sharma, 1974), for modifying their Utah smelter to a version of the Noranda concept suggest that this assumption is justified.

It should also be noted that the capacity of the plant is increased by oxygen enrichment. The degree to which blast air should be enriched is subject to a number of parameters, not all of which are obvious. However, in view of the fact that enriching the air to 35% oxygen doubles the capacity of the Noranda reactor, it is safe to say that the Noranda process using enriched air is less expensive, in terms of capital cost per unit of output, than the conventional smelting process of the same capacity.

Table IV-24 shows estimates of capital and operating costs for the Noranda process based on about 25% oxygen enrichment. This degree of oxygen enrichment has been used for several campaigns on the Noranda reactor and represents the oxygen usage when the plant capacity is about 100,000 ton/yr. (The same degree of enrichment has been used for the evaluation of the Mitsubishi process in Section E.) Higher degrees of enrichment raise the temperature of the bath and increase refractory wear to an intolerable extent.

An unusual feature of the Noranda reactor is the maintenance requirements. Maintenance costs are high and more critical with the Noranda process than with the reverberatory process. Downtime schedules for repair are projected to be the following:

TABLE IV-24

OPERATING COSTS: NORANDA (MATTE) PROCESS
(Basis: Copper sulfide concentrates, 28.6% Cu, 29.3% Fe, 33.4% S
100,000 ton/yr of copper; 25% O_2 enrichment)

	Unit	$/Unit	Units/Ton	$/Ton Cu
CAPITAL INVESTMENT (CI) $/annual ton			$750	
OPERATING COSTS				
VARIABLE COSTS				
Silica Flux	ton	8.00	0.86	6.88
Limestone	ton	10.00	---	---
H_2SO_4 Credit	ton	10.00	3.33	(33.30)
Oxygen	ton	15.00	0.29	4.35
Fuel Oil	10^6 Btu*	2.00	6.5	13.0
Natural Gas	10^6 Btu	0.65	1.3	0.85
Coal	10^6 Btu	0.70	2.5	1.75
Electricity	kWh	0.021	366.4	7.69
Water: Process	10^3 gal**	0.02	1.06	0.21
Cooling	10^3 gal	0.05	2.0	0.10
Refractories	ton	300.00	0.025	7.50
Direct Operating and Maintenance Labor (L)	Man-hr	5.75	6.2	35.65
Supervision (S)	L	15% L	---	5.35
Maintenance Materials	CI	4% CI	---	30.00
Labor Overhead	L+S	35% (L+S)	---	14.35
TOTAL VARIABLE COSTS				94.38
FIXED COSTS				
Plant Overhead	L+S	65% (L+S)	---	26.65
Local Taxes & Insurance	CI	2% CI	---	15.00
Depreciation	CI	7% CI	---	52.50
Capital Recovery	CI	20% CI	---	150.00
TOTAL FIXED COSTS				244.15
TOTAL COSTS				341.53

---

*M = 10^6
**MM = 10^3

16 days for every 72 days of continuous copper making

20 days for every 120 days of continuous matte making

The reactor has to be partially or totally relined during that time. However, at this time there is a high degree of uncertainty in these figures. Once a commercial plant starts operating, better data should become available.

b. Comparison with the Base Line

(1) Energy Use

Table IV-24 shows that energy use is decreased for the Noranda process. As mentioned in Section C, there is no unique conservation in energy form achievable with any of the new smelting processes.

It should be noted that the Noranda reactor is fitted with a main burner at the feed end and a secondary burner at the slag tapping end. The heat transfer from the flames to the bath is not optimum; the heat transfer is favored in the vicinity of the main burner. Most of the heat is taken by the nitrogen present in the air reacting with the fuel, and goes up to the hood. One way to distribute the heat generated by extraneous fuels better is to mix carbon with the feed in the form of coal or coke particles; 3% of the required fuel is presently injected with the feed to the Noranda reactor in the form of low quality, high sulfur coal. Table IV-24 takes this into account.

(2) Pollution Aspects

The Noranda smelter and its associated acid plant recover a higher amount of SO_2 (over 90%) compared to conventional smelting (50-70%). Table IV-25 shows the total pollution control costs and assumes conversion to sulfuric acid.

(3) Cost Comparison

Comparison of Tables IV-6 and IV-24 shows that the cost of Noranda smelting is lower because of its higher energy efficiency.

TABLE IV-25

COST OF POLLUTION CONTROL IN THE NORANDA SMELTING PROCESS

	Units	$/Unit	Units/Ton	$/Ton of Copper
Acid Manufacture	Ton	18.88	3.33	62.87
Credit for Acid Sales	Ton	(10.00)	3.33	(33.30)
Water Pollution	Ton	-	-	3.25
Slag Disposal (Tailings)	Ton	0.63	3	1.90
Dust Disposal[1]	Ton	24.00	0.02	0.48
Total Smelting and Converting Pollution Costs				35.30

---

[1] The same amount of discarded dust is shown as for the conventional smelters.

E. THE MITSUBISHI PROCESS

1. Concept and Operations

a. Description

The Mitsubishi process consists of three metallurgical stages, each of which is carried out in a separate furnace (Figure IV-11). Thus, there is a smelting furnace for concentrates, a converting furnace to oxidize iron in the matte and make blister copper, and a slag-cleaning furnace. Intermediate products in the molten state move continuously among the respective furnaces, which are thus functionally connected with each other.

Copper concentrates, fluxes, and oxidizing air are charged into the smelting furnace through lances installed vertically through the roof of the furnace and reaching just above the bath surface. Use of the lances, says Mitsubishi, brings about a high smelting and oxidation rate and simplifies furnace design and maintenance. Another advantage of this top-blowing method is that, when necessary, oxygen or fuel oil can also be introduced through the lances. Table IV-26 shows typical blowing conditions through the lances in the smelting furnace of the Onahama pilot plant.

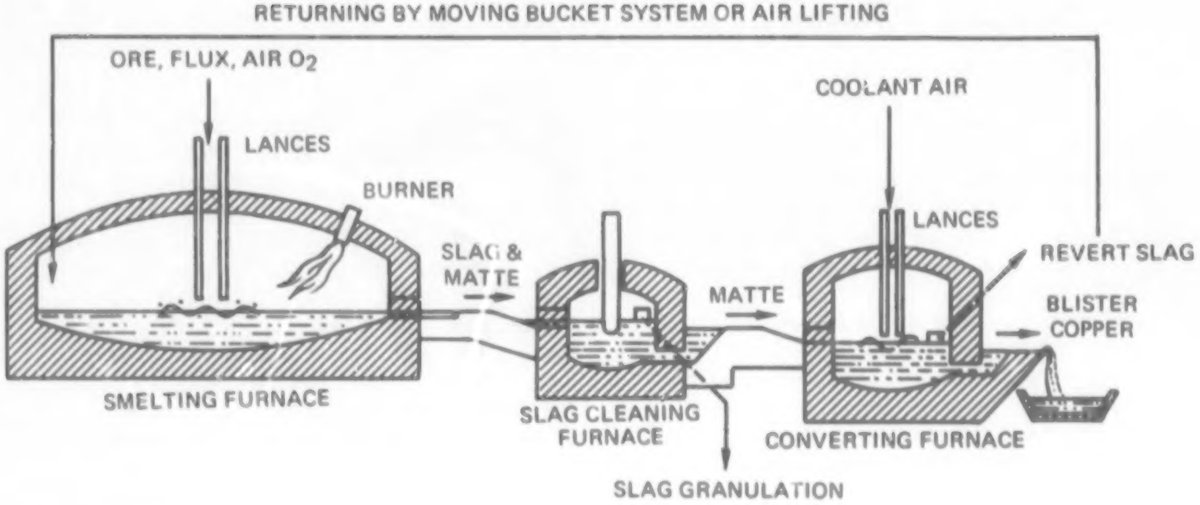
The matte and slag produced during smelting continuously flow to the slag-cleaning furnace as a dispersion of matte drops in the slag. Here, after being cleaned, the slag is skimmed out continuously to be granulated (average copper content of this waste slag is about 0.4%), while the matte is sent to the converting furnace.

In the converting furnace, which is also equipped with lances that introduce blow air, matte undergoes oxidation to blister copper. This blister copper is continuously tapped out of the furnace and any slag formed during the converting stage is returned to the smelting furnace via a moving bucket system.

b. Pilot Plant Results

To establish basic operating techniques, Mitsubishi initially conducted its test campaigns in the pilot plant by combining the smelting and "converting" furnaces to obtain white metal: i.e., matte containing about 80% copper and no iron. Soon afterward, the degree of oxidation was increased and production of blister copper was started in the converting furnace. Table IV-27 shows the composition of various types of concentrates smelted during four campaigns; the fluxes used at the time were silica (85-90% SiO_2, 4-4.5% Al_2O_3) and limestone (53-55% CaO, 1-2% SiO_2).

Mitsubishi reports that the daily smelting rate of its pilot plant operation varied between 5 and 6 mt/m^3 of furnace volume. Such a high smelting rate--about six times greater than that of a reverb, and at least twice as much as that of a flash smelting furnace (Table IV-28)--is achievable for two reasons. First, each furnace has only a single reaction zone, and the smelting rate can thus be increased far more than would be possible in a furnace


RETURNING BY MOVING BUCKET SYSTEM OR AIR LIFTING
ORE, FLUX, AIR O_2
LANCES
BURNER
SLAG & MATTE
MATTE
COOLANT AIR
LANCES
REVERT SLAG
BLISTER COPPER
SMELTING FURNACE
SLAG CLEANING FURNACE
CONVERTING FURNACE
SLAG GRANULATION

SOURCE: E&MJ, August 1972.

Figure IV-11. Schematic View of Mitsubishi's Semi-Commercial Plant

TABLE IV-26

BLOWING CONDITIONS

Smelting Furnace	
Feed rate of concentrates, mtph	3.0
Blowing rate, Nm^3/hr	2,000-3,000
Oxygen mixed to the blow air, Nm^3/hr	200-300
Combustion rate of fuel oil, liters per hr	150-200
Air for fuel oil combustion, Nm^3/hr	1,500-2,000
Converting furnace	
Blowing rate, Nm^3/hr	1,000
Oxygen mixed to the blow air, Nm^3/hr	20-50
Combustion rate of fuel oil, liters per hr*	20

*In the converting furnace of the pilot plant, the furnace temperature could not be maintained by matte converting alone, owing to the relatively small heat generation. Fuel oil and oxygen were, therefore, blown through the same lances with the blow air. In a commercial furnace having a larger capacity, the heat generated by converting would be sufficient enough to maintain the temperature of the melts.

Source: E&MJ, August 1972

TABLE IV-27

AVERAGE COMPOSITIONS AND THROUGHPUT OF CONCENTRATES

Campaign	A	B	C	D[3]
Duration, hr	384	235	791	530
Concentrates fed, mt	1,031	632	2,102	1,392
Avg. feed rate, mtph[1]	2.69	2.69	2.66	2.62
Average compositions of concentrates, %				
Cu	19.4	19.6	20.9	23.1
Fe	23.3	23.6	25.2	24.5
S	29.4	29.1	28.0	30.8
Pb	2.3	1.9	0.4	tr.
Zn	6.6	7.8	1.2	0.2
SiO_2	14.2[2]	12.6[2]	15.5[2]	7.5
Al_2O_3	1.3	2.6	2.9	0.1

(1) Average feed rate was smaller than design capacity because of the downtime for cleaning of the flues and some improvement works.
(2) These high values are due to silica sand mixed to the concentrates.
(3) The slag formed in the converting furnace was not returned to the smelting furnace except for campaign D.

Source: E&MJ, August 1972

TABLE IV-28

SMELTING RATE AND FUEL CONSUMPTION OF VARIOUS SMELTERS

Process	Smelting rate, $mtpd/m^3$ of furnace volume	Fuel consumption, kg oil per mt concentrate
Smelting furnace		
Low-grade matte (40% Cu)[1]	4.7	145
High-grade matte (70% Cu)[1]	6.0	82
High-grade matte (60% Cu)[2]	5.5,6.0	35-50
Reverberatory furnace		
Green charge, Onahama[3]	0.8	160
Calcine charge, Naoshima[4]	1.0	120
Flash smelting furnace		
Ashio[5]	2.0	50

(1) These are the results of relatively short campaigns carried out at the earlier period of this project, using a smelting furnace of somewhat different design. Oxygen was not used.

(2) Oxygen of about 80 Nm^3 ton conc. was added to the blow air.

(3) Combustion air is preheated to 300-350°C.

(4) The temperature of calcine is about 650°C.

(5) Estimated from the published data.

Source: E&MJ, August 1972

with two reaction zones, e.g., oxidation and settling, since oxidation is promoted by good mixing but settling requires quiescent conditions. Second, the concentrates and fluxes, injected into the bath through the lances, are smelted so promptly that the reaction heat generated by the oxidation of sulfur and iron can be used effectively.

The composition range of slag formed in the smelting furnace was 30-35% SiO_2, 5-7% CaO, 2-6% Al_2O_3, and 40-45% Fe and Zn. The slag was fluxed to obtain an Al_2O_3/CaO ratio of less than 1.0. Copper content in the slag tapped from the slag-cleaning furnace during campaign "C" is shown in Figure IV-12 plotted against the matte grade. As Figure IV-12 indicates, the slag factors (apparently defined as 100 times % copper in slag/% copper in matte) are distributed mostly between 0.7 and 1.0--whereas, in a conventional reverberatory practice, slag factors are usually between 1.0 and 1.5. Table IV-29 shows copper losses in the slag before and after cleaning.

c. Converter Slag

Copper content of matte entering the converting furnace varied from 57% to 63%. Typical compositions of the converting furnace slag were as follows: 7-15% Cu, 40-50% Fe, 10-20% SiO_2 plus CaO. (Limestone was added to the slag to obtain good fluidity.) Analysis of the slag also showed that 40-60% of copper content in the slag was metallic and sulfide copper and the rest was oxide. Most of the slag's iron content was in the form of magnetite. Before being charged into the smelting furnace, the converting furnace slag was cooled and crushed. In the larger plant the slag is granulated, dried, and returned to the furnace. Slag recirculation has no significant influence on copper losses in the smelting furnace slag.

d. Blister Cooper

Typical analyses of blister copper, shown in Table IV-30, indicate a copper content varying from 98-99% and a sulfur content of 0.4-0.8%. This sulfur content was lower than in the blister copper that would be produced in a furnace having three separate phases (i.e., slag, white metal or low iron matte and copper phases). The low sulfur content in Mitsubishi's blister copper seems to indicate that the converting furnace was operated under such conditions that no matte layer existed as a separate phase between the slag and copper phases. Otherwise, the blister copper would be nearly sulfur saturated.

Other impurities such as Pb, As, and Sb were present but in small amounts.

e. Flue Dusts

Since the concentrates injected through the lances in the smelting furnace were readily and promptly captured by the bath, the amount of mechanical flue dusts was small--or nearly proportional to the Pb and Zn content of the concentrates. These dusts, collected in the cooler, were sent back to the process. Dusts rich in Pb and Zn were sent to a lead-zinc smelter.

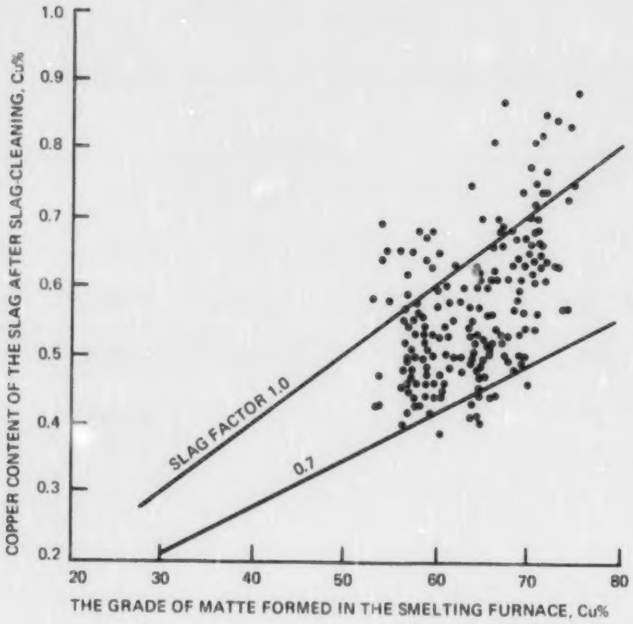


Figure IV-12. Copper Losses in Smelting Furnace Slag

TABLE IV-29

COPPER LOSSES IN SLAG

	% Cu in Slag	
Sample No.*	Before Cleaning	After Cleaning
1	1.53	0.83
2	0.69	0.43
3	0.82	0.42
4	0.80	0.35
5	0.77	0.49
6	1.21	0.45
7	0.92	0.49

---

[*] Sampling interval was one hour.

TABLE IV-30

TYPICAL ANALYSES OF BLISTER COPPER PRODUCED

	Analysis %				
Campaign	Cu	S	Pb	Fe	Zn
A	98.0	0.6-0.7	0.22*	0.08	0.05
B	98.0	0.6-0.8	0.50*	0.001	-
C	98.5	0.4-0.8	0.05	0.008	-
D	99.0	0.7-0.8	0.01	0.004	-

---

*These high values are due to the high Pb contents in the concentrates.

2. Current Status

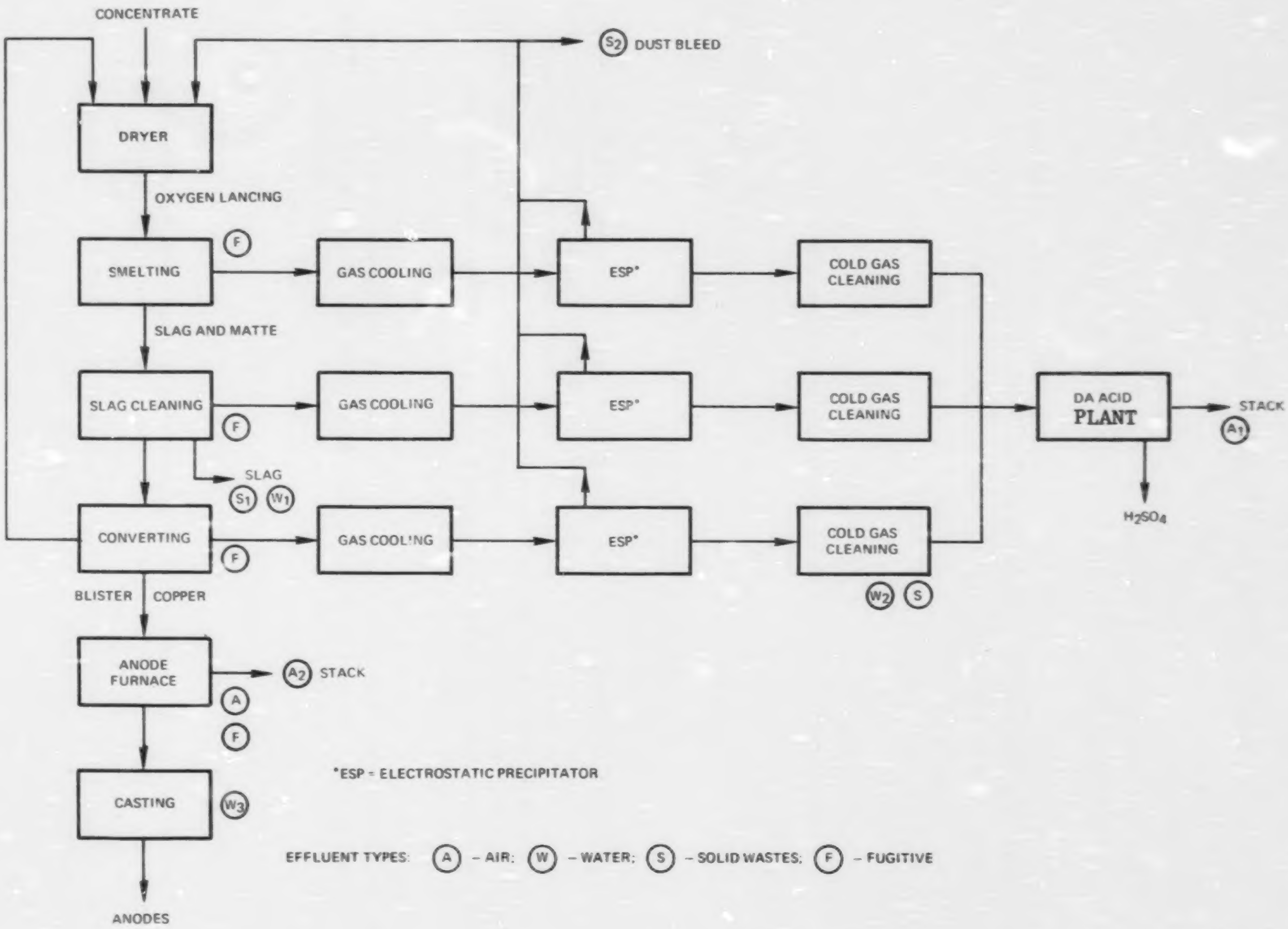
Development work on this process began in 1961. After a series of preliminary experiments, Mitsubishi constructed a prototype pilot plant with a monthly capacity of 500 tons of blister copper at the Onahama smelter. Ishikawajima-Harima Heavy Industries was involved in this development work. When pilot plant operations proved the technical feasibility of the process, Mitsubishi decided to build a semi-commercial plant having a capacity of 1,500 metric tons/month of blister copper. This semi-commercial plant has been on stream since November 1971. A commercial operation producing 50,000 ton/yr of blister copper is now being started at Naoshima and a 130,000 ton/yr plant is being designed by Montreal's SNC Consultants for the Kidd Creek smelter of Texasgulf.

3. Effluent Control

Figure IV-13 is a schematic flow diagram of copper smelting using the Mitsubishi process. The emission sources of pollutants are identified in four categories: air, solid, water, and fugitive. Except for the slag treatment method, the pollution controls required are identical to those necessary for the Outokumpu flash smelting process. Table IV-31 shows the magnitude of these streams and the major constituents.

a. Air

Upon leaving any of the three furnaces, the mixed off-gases are expected to average over 10% SO_2 when the smelting furnace is operated with air enriched


CONCENTRATE
S2 DUST BLEED
DRYER
OXYGEN LANCING
SMELTING
F
GAS COOLING
ESP*
COLD GAS CLEANING
SLAG AND MATTE
SLAG CLEANING
F
GAS COOLING
ESP*
COLD GAS CLEANING
DA ACID PLANT
STACK
A1
H_2SO_4
SLAG
S1
W1
CONVERTING
F
GAS COOLING
ESP*
COLD GAS CLEANING
W2
S
BLISTER COPPER
ANODE FURNACE
A2 STACK
A
F
CASTING
W3
ANODES

*ESP = ELECTROSTATIC PRECIPITATOR

EFFLUENT TYPES: Ⓐ – AIR; Ⓦ – WATER; Ⓢ – SOLID WASTES; Ⓕ – FUGITIVE

Figure IV-13. Emission Sources in the Mitsubishi Continuous Copper Smelting Process

TABLE IV-31

EMISSIONS FROM THE MITSUBISHI PROCESS

Stream	Stream Size	Major Constituents
• Air Pollution		
A-1 - Acid Plant Tail Gas	55,000 scfm	SO_2 - 0.05%
A-2 - Anode Furnace Gas	NA*	Flue Gas, Some SO_2
• Water Pollution		
W-1 - Slag Granulation	50,000 liter/10^3 kg	TDS, TSS
W-2 - Acid Plant Blowdown	14,000 liter/10^3 kg	TPS, TSS, Acidity
W-3 - Contact Cooling	7,800 liter/10^3 kg	TDS, TSS
• Solid Wastes		
S-1 - Cleaned Slag	3 ton/ton copper	Iron Silicates
S-2 - Dust Bleed	0.3 ton/ton copper	Copper Oxides, Minor Elements
• Fugitive Emissions	NA*	

* NA = not available

to 25% oxygen. This steady, high SO_2 gas generation is a significant advantage over the conventional reverberatory process, as sulfur can be readily recovered as sulfuric acid. Since the molten liquids flow continuously over very short distances, minimum air pollution is generated in transfer operations, and "converter aisle losses" typical of conventional operations are avoided. Thus, fugitive emissions are expected to be lower than for conventional or for Outokumpu and Noranda (matte) processes.

After cooling and dry cleaning in electrostatic precipitators or fabric filters operated above the dew point, the collected off-gases usually require a wet cleaning stage to remove any fine particulates and excess moisture. The cleaned gases are then admitted to a double contact acid plant for H_2SO_4 manufacture. The total sulfur recovery is over 90%, as with all these advanced pyrometallurgical processes.

b. Solid Wastes

The converter slag is entirely returned to the smelting furnace, so that the only slag to be disposed of comes from the slag-cleaning furnace. About three tons of granulated slag per ton of anode copper produced must be landfilled at a cost of about $5/ton. The total cost incurred to a smelter producing 100,000 ton/yr of anode copper is therefore $1,500,000/yr.

Flue dusts are generated from all three furnaces in amounts expected to be a little smaller than obtained in flash smelting. The dusts are normally concentrated in volatile impurities and have to be bled to the extent necessary to avoid impurity build-up. The remaining dust is recycled. The cost of disposing of dusts is the same as for the base line - $24/ton of dust.

A schematic illustration of the flows of minor elements in a Mitsubishi smelter is shown on Figure IV-14. When making matte containing 60% copper, one may estimate that a great similarity exists between this process and the Outokumpu flash smelting process. Distribution of impurities in these streams is not yet known, although it is expected to be similar to that from the flash smelting process.

c. Water

The water effluent streams in the Mitsubishi process are those associated with the acid plant, anode cooling, and slag granulation. These streams are identical to those discussed earlier for the Outokumpu process.

4. Technical Considerations

a. Impurities

By the nature of the process, the impurity distributions in the Mitsubishi process appear to be somewhat similar to those in Outokumpu flash smelting. One would expect precious metals to be retained in the metal. Cobalt, tin, and nickel would tend to be retained in the matte due to the reducing conditions of the electric furnace. Zinc and lead would be volatilized and recovered mainly in the dusts of the settler. Figure IV-15 shows the distribution of lead and zinc between matte and slag. Selenium and tellurium will follow the sulfur in the matte. Arsenic, tin, and antimony will tend to be recovered as oxides in the dusts of the smelting furnace; the dusts from the converting furnace will contain more bismuth, lead, antimony, selenium, and tellurium.

5. Economic Factors

a. Capital and Operating Costs

Table IV-32 shows estimates of capital and operating costs (including pollution control costs) for the Mitsubishi process based on about 25% oxygen enrichment--the same degree of enrichment assumed in the Noranda process. A lime slag is also assumed for the converting reactor.

b. Comparison with the Base Line

(1) Energy Use

Table IV-32 shows that energy use is reduced from 18.6 to 9.8 million Btu/ton of fossil energy. As mentioned in Section C, there is no further conservation of energy form since coal, oil, or gas can be used with any of the new smelting processes.

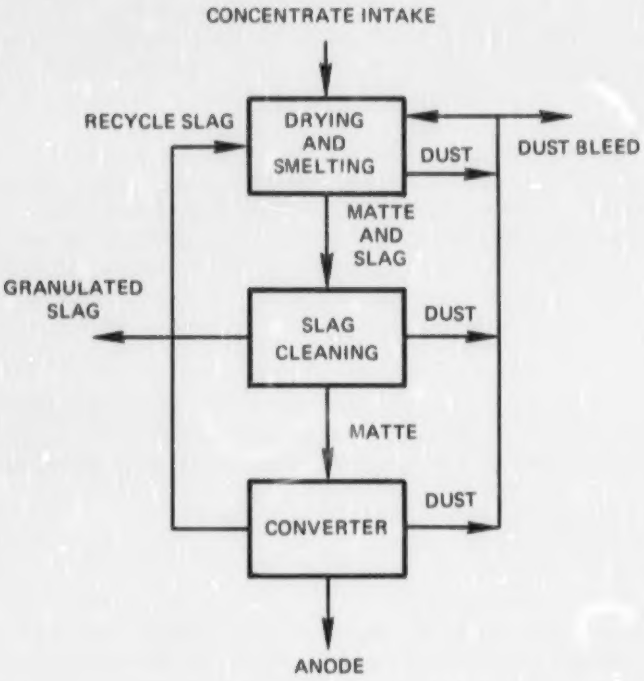

CONCENTRATE INTAKE
RECYCLE SLAG
DRYING AND SMELTING
DUST
DUST BLEED
MATTE AND SLAG
GRANULATED SLAG
SLAG CLEANING
DUST
MATTE
CONVERTER
DUST
ANODE

Figure IV-14. Diagram of Impurity Flow Within a Smelter Using the Mitsubishi Process

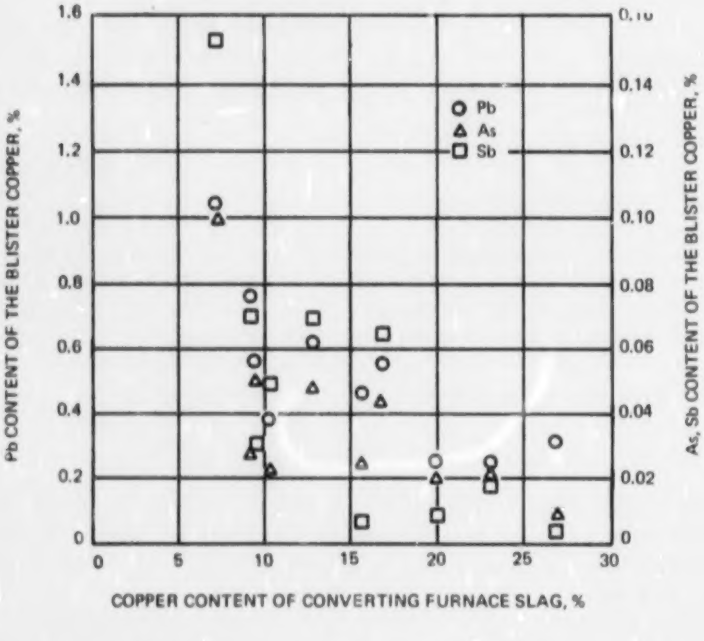


Figure IV-15. Slag Composition and Impurity Levels

TABLE IV-32

OPERATING COSTS: THE MITSUBISHI PROCESS

	Unit	$/Unit	Units/ton	$/ton Cu
CAPITAL INVESTMENT (CI) $/annual ton			$750	
OPERATING COSTS				
VARIABLE COSTS				
Silica Flux	ton	8.00	0.86	6.88
Limestone	ton	10.00	0.118	1.18
H_2SO_4 credit	ton	10.00	3.33	(33.30)
Oxygen	ton	15.00	0.3	4.35
Fuel Oil	10^6 Btu	2.00	8.5	17.00
Natural Gas	10^6 Btu	0.65	1.3	0.85
Coal	10^6 Btu	0.70	-	-
Electricity	kWh	0.021	366.4	7.69
Water: Process	10^3 gal	0.02	1.06	0.21
Cooling	10^3 gal	0.05	2.0	0.10
Refractories	ton	300.00	0.014	4.20
Direct Operating and Maintenance Labor (L)	Man-hr	5.75	6.2	35.65
Supervision (S)	L	15% L	-	5.35
Maintenance Materials	CI	4% CI	-	30.00
Labor Overhead	L+S	35% (L+S)	-	14.35
TOTAL VARIABLE COSTS				94.51
FIXED COSTS				
Plant Overhead	L+S	65% (L+S)	-	26.65
Local Taxes & Insurance	CI	2%	-	15.00
Depreciation	CI	7% CI	-	52.50
Capital Recovery	CI	20% CI	-	150.00
TOTAL FIXED COSTS				244.15
TOTAL COSTS				338.66

(2) Pollution Aspects

The Mitsubishi smelter and its associated acid plant recover a higher amount of SO_2 (over 90%) than does conventional smelting (50-70%). Table IV-33 shows the pollution control costs. These are about 14% of the total smelting costs.

The Mitsubishi process potentially has less problems with fugitive emissions than other new processes since all the transfer points are covered and hooded.

(3) Cost Comparison

Comparison of Tables IV-6 and IV-32 shows that the cost of the Mitsubishi process is lower than for the conventional smelting primarily because of its increased energy efficiency. Also, because the process employs a different smelting and converting unit, it should be more flexible in its ability to treat impure concentrates.

TABLE IV-33

COST OF POLLUTION CONTROL IN THE MITSUBISHI CONTINUOUS COPPER SMELTING PROCESS

	Units	$/Unit	Units/Ton	$/Ton of Copper
Acid Manufacture	Ton	18.88	3.33	62.87
Credit for Acid Sales	Ton	(10.00)	3.33	(33.30)
Water Pollution	Ton	-	-	3.25
Slag Disposal (Granulation)	Ton	5.00	3	15.00
Dust Disposal	Ton	24.00	0.02	0.48
Total Smelting and Converting Pollution Costs				48.30

F. THE USE OF OXYGEN IN SMELTING

1. Concept and Operations

Copper smelting can be conducted with pure oxygen or by using oxygen-enriched air. Reasons for using oxygen or oxygen enrichment include:

- Increasing processing temperatures and process heat rates.
- Decreasing the nitrogen content of the flue gases (when high SO_2 concentrations are needed) and increasing fuel efficiency (particularly where waste heat is not recovered).

- Increasing the specific capacity of furnaces so that production of metal is increased significantly for a given size of reactor.

Examples of the above in copper smelting are as follows:

- Fuel efficiency in conventional reverb smelting can be increased with oxygen enrichment. The limitations on oxygen use arise from the decrease in refractory life as operating temperature increases. Considerations of refractory wear normally limit the enrichment of converter air to about 27% oxygen for conventional bottom-blown converters. The enrichment not only increases SO_2 concentrations but also increases the scrap melting capability of the converter.

- Furthermore, since the sensible heat in converter gases is not usually recovered, and less nitrogen has to be heated to exit gas temperatures, there is a significant saving in energy. The net heat generation under these conditions can be used for melting scrap (Parameswaran and Nadkarni, 1975). The converter is an ideal unit for melting and refining several types of low-grade copper scrap which are not normally handled by the secondary copper industry.

- The specific capacity of furnaces such as the flash smelting furnaces can be increased by the use of oxygen. In this case, the increase in energy efficiency is not as great as in the case of converter operations since waste heat recovery is already practiced. However, the increase in smelting rate significantly decreases the capital costs per unit of output. This is advantageous for new plants and extremely attractive for existing plants which need to increase production with normal capital outlay.

- We have chosen the example of Outokumpu flash smelting to illustrate the beneficial effect of oxygen use in copper smelting.

2. Current Status

Oxygen enrichment of Outokumpu furnace gases has been practiced since about 1972 at Harjavalta. This has enabled almost completely autogenous operations of the furnace and resulted in a large increase in furnace capacity.

3. Effluents

An oxygen plant is a user of significant quantities of cooling water for indirect cooling but produces no known deleterious effluents. Cooling tower blowdown will contain oil and grease, corrosion inhibitors, and chlorides concentrated from the feed water. The plant consumes electricity, and the generation of this electricity at a central power station has the associated pollution consequences; however, these problems are readily identifiable and are not considered further in this study.

As far as smelter effluents are concerned, we believe that the use of oxygen will not significantly change the nature and amount of the effluent and Table IV-9 will still apply.

Because of higher operating temperatures, the generation of smelter dusts might increase, resulting in an increased circulating dust load, however, there do not appear to be any published data in this area. Higher furnace temperatures might also result in more NO_x formation in the furnace. However, since furnace gases are scrubbed and treated in the acid plant, these nitrogen gases are probably absorbed in the acid, as occurs in the Guy-Lussac towers in the chamber process for making sulfuric acid. There are no published data in this area.

4. Technical Considerations

Interplay of air preheating temperature and oxygen enrichment in Figure IV-16 illustrates the effect of the process air preheating temperature or oxygen enrichment on the net energy consumption. As it appears from this figure, a change in either of the above-mentioned two factors is of minor importance only, because the lower the preheating temperature or the percentage of oxygen enrichment, the greater the amount of oil required for smelting, which in turn means increased off-gas amount and waste-heat credit. However, the figures given indicate that an increase in the process air preheating temperature somewhat decreases the overall net energy requirements in smelting provided that the thermal efficiency of the air preheater is adequate. The use of oxygen does not lead to an improved saving of energy but it reduces the consumption of extraneous fuel and considerably increases the smelting capacity.

The flash smelting furnace capacity can be increased by raising either the preheating temperature of process air or the percentage of oxygen enrichment. The simultaneous raising of the preheating temperature and oxygen enrichment rapidly decreases the off-gas flow and gives more capacity. Once the autogenous point of the reaction shaft is reached, this point cannot be exceeded without overheating the reaction shaft. In such a case, increase in capacity by the use of additional oxygen is possible only if the process air temperature is lowered.

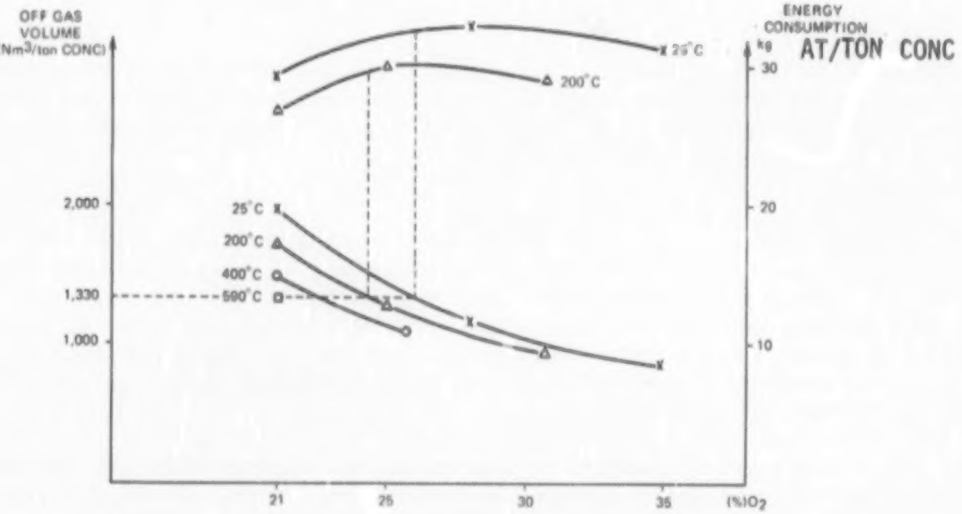


Figure IV-16. Off-Gas Volume and Energy Consumption at the Harjavalta Copper Smelter

5. Economic Factors

a. Capital and Operating Costs

Table IV-34 presents estimated capital and operating costs (including pollution control) for the Outokumpu process using air and using about 35% oxygen (autogenous operation in the reaction shaft). The table shows that the operating costs decreases mainly because of lower fixed costs. In Table IV-34, we have shown oxygen as a raw material purchased from an "across the fence" plant. If the cost of such a plant were included in the fixed charges, one would still show a saving in operating cost.

G. METAL RECOVERY FROM SLAG

1. Background

a. Introduction

In conventional copper smelting, converter slag is recycled to the reverb and all the slag tapped from the reverb is discarded. The copper contained in this discard slag is lost. The amount of copper lost with the slag is quite significant, about 1.5-3% or more of the copper in the feed materials.

It is well known that the concentration of copper in the reverb slag varies directly with matte grade (see Figure IV-17). With newer processes where there is significant sulfur oxidation in the smelting step, the matte grades are higher and consequently the concentration of copper in the slag is also higher (explained in b). The oxidation of sulfur in the smelting step is beneficial from a pollution control viewpoint since the off-gases from these smelting units contain 10-15% SO_2 (suitable for sulfuric acid manufacture) compared to SO_2 concentrations of 1-2% normally found in reverb gases. However, the slag contains an unacceptable high concentration of copper and cannot be discarded. The availability of technology for metal recovery from slag has made it possible to smelt at high matte grades, recover much of the copper in the slag, and produce a slag stream that can be discarded without undue economic penalty. Thus, these processes for recovering metal from slag are considered an essential factor in all of the new smelting technologies.

b. Mechanism of Metallic Losses in the Slag

In copper pyrometallurgy, the molten feed materials separate into two phases - slag and matte. The distribution of copper between these phases is determined by solubility, kinetic factors, surface phenomena, and other parameters governing the separation of the melt into two distinct phases:

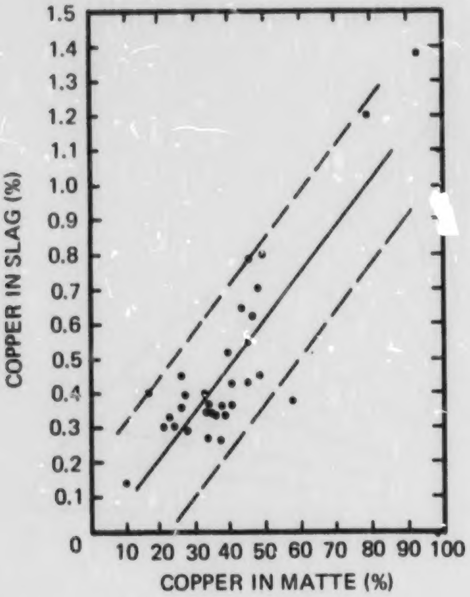
- The liquid phases have some limited mutual solubility: part of the copper and other metallic values are chemically "lost" by solution to the slag phase. The amount and nature of these losses are governed by the thermodynamics of the system, and our knowledge of the chemistry of this process is still incomplete. Sulfides, oxides, and elemental copper are partially soluble in fayalite slags in contact with copper mattes.

TABLE IV-34

OPERATING COSTS: OUTOKUMPU FLASH SMELTING USING AIR AND 35% OXYGEN

(Basis: Copper sulfide concentrates, 28.6% Cu, 29.3% Fe, 33.4% S
Initial unit built for 100,000 ton/yr of copper)

			Without Oxygen		With Oxygen (35% enrichment)	
	Unit	$/Unit	Units/ Ton	$/Ton Cu	Units/ Ton	$/Ton Cu
CAPITAL INVESTMENT (CI)	$/annual ton			$750		$500
OPERATING COSTS						
VARIABLE COSTS						
Silica Flux	ton	8.00	0.86	6.88	0.86	6.88
H_2SO_4 Credit	ton	10.00	3.33	(33.30)	3.33	(33.30)
Oxygen	ton	15.00	---	---	1.3	19.50
Fuel Oil	10^6 Btu	2.00	12.7	25.40	5.9	11.80
Natural Gas	10^6 Btu	0.65	1.3	0.85	1.3	0.85
Electricity	kWh	0.021	366.4	7.69	366.4	7.69
Water: Process	10^3 gal	0.02	1.06	0.21	1.06	0.20
Cooling	10^3 gal	0.05	2.0	0.10	2.0	0.10
Refractories	ton	300.00	0.014	4.20	0.014	4.20
Direct Operating and Maintenance Labor (L)	Man-hr	5.75	6.2	35.65	6.2	35.65
Supervision (S)	L	15% L	---	5.35	---	5.35
Maintenance Materials	CI	4% CI	---	30.00	---	20.00
Labor Overhead	L+S	35% (L+S)	---	14.35	---	14.35
TOTAL VARIABLE COSTS				97.38		93.28
FIXED COSTS						
Plant Overhead	L+S	65% (L+S)	---	26.65	---	26.65
Local Taxes & Insurance	CI	2% CI	---	15.00	---	10.00
Depreciation	CI	7% CI	---	52.50	---	35.00
Capital Recovery	CI	20% CI	---	150.00	---	100.00
TOTAL FIXED COSTS				244.15		171.65
TOTAL COSTS				341.53		264.93

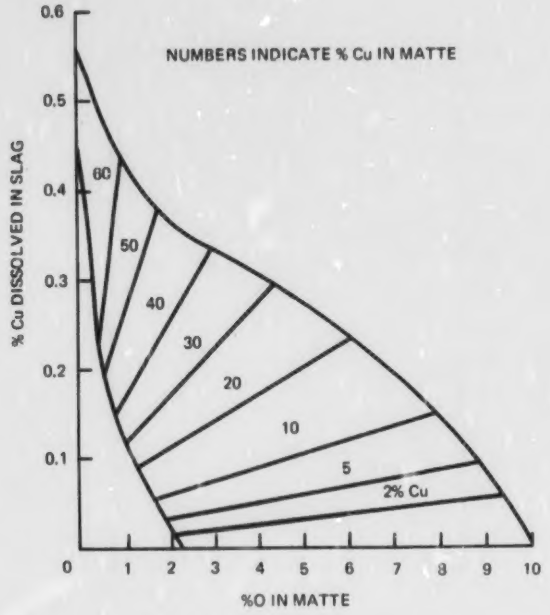


SOURCE: Ruddle, 1953.

Figure IV-17. Copper Content of Reverberatory Slags Plotted Against Matte Grade

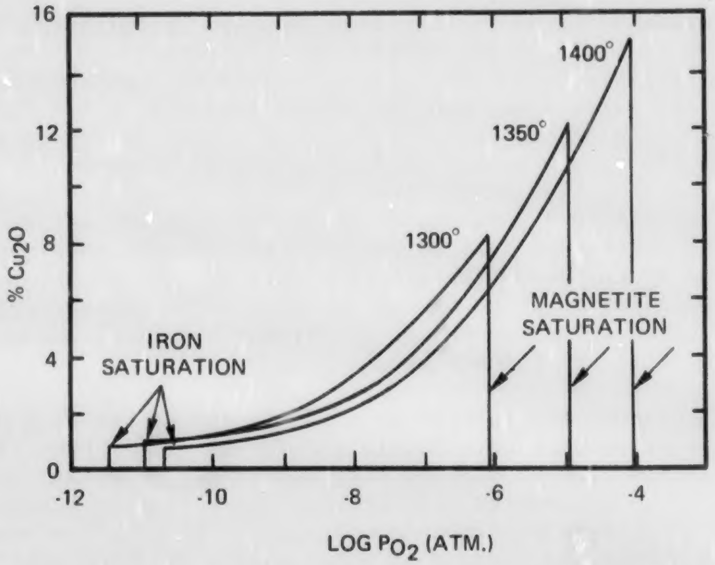
The best correlation so far has been proposed by Spira and Themelis (1969). Their findings are summarized in Figure IV-18. The most important variables governing the solubility of copper in fayalite slags are the matte grade and the oxygen potential. The higher the matte grade, the higher the solubility of copper in the slag. Also, the higher the oxygen potential for a given matte grade, the higher the copper loss in the slag. The practical consequence is that processes operating at high matte grade and high oxygen potential (continuous processes, late stage of converting) enhance the chemical dissolution of copper in the slag. Figure IV-18 also shows the theoretical limit to which a slag can be cleaned of its copper content at a given oxygen potential by pyrometallurgical techniques such as electric arc furnace settling.

Copper is believed to dissolve as oxide (Cu_2O) in the slag during the later stage of converting. Ruddle and Taylor (1966) have proposed the correlation between Cu_2O in slag and oxygen potential in the Cu-Fe_2O_3-$FeCO_3$-SiO_2 system. Their findings appear in Figure IV-19. Copper is not the only element chemically soluble in the slag. Some ores contain sizeable amounts of other easily-oxidized metals. The oxides of lead, zinc, tin, nickel, and cobalt are highly soluble in fayalite; oxidizing conditions also favor their retention in the slag. This is one way in which impurities leave the system.



SOURCE: Spira and Themelis, 1969.

Figure IV-18. Solubility of Copper in Silica-Saturated Slag as a Function of Oxygen and Copper Content of Matte



SOURCE: Ruddle and Taylor, 1966.

Figure IV-19. Effect of Oxygen Pressure on Cu_2O Content of Slag

- The separation of the slag phase and matte (or copper) phase is slowed down by the combined action of several physical parameters: turbulence, viscosity of the slag, surface tension, and gravity.

  During the smelting operation, droplets of matte coalesce and sink to the bottom of the furnace to form the matte layer. The violent turbulence created by submerged gas injection as well as the sulfur dioxide evolution from the matte or copper phase tend to promote a certain amount of dispersion, carrying droplets of copper or matte into the slag. This tendency of matte particles to become buoyant is favored by increased matte grade. The settling speed is also fairly dependent on the slag viscosity, which in turn depends on the silica content of the slag (higher silica means higher viscosity). As it turns out, this mechanical entrapment of copper and other metallic values in the slag accounts from anywhere between 25 and 75% of the losses occurring during converting or under other turbulent conditions.

  Copper mattes contain other valuable elements, in addition to copper. By the same entrapment mechanism, proportional amounts of gold, silver, platinum, etc. are retained in the slag.

Flash smelting slags contain 1-2% copper, because the fast smelting rate does not allow sufficient time for settling and the finer matte-droplets disperse in the slag. Converter slags may contain from 3-6% copper in most cases, depending on the practice followed. The Noranda reactor slag contains from 6-7% copper when making matte, and 10-12% copper when making copper.

2. Slag Cleaning Via Flotation

a. Concept and Operation

(1) Slag Composition

The presence of sufficient amounts of silica is a requirement for copper smelting, since silica is the fluxing agent that ties up iron in the concentrate as iron silicate. However, silica is a strong glass-forming component, and therefore low-silica slags (20-25% SiO_2) are preferable in the milling process because they are easier to grind. Also, there is less slag produced per ton of concentrate smelted. Ultimate copper loss in discard slag is proportional to the quantity of slag, hence there is incentive to minimize slag quantity.

Alumina and lime also tend to promote the formation of the amorphous, vitreous phase and thus inhibit the precipitation of copper sulfide particles. Zinc in the slag above the 6% level has the same effect.

"Magnetite" amounts to a sizeable percentage of converter and oxygen smelting slags, sometimes up to 30%. One advantage of the milling and flotation process over simple recycling to the smelting furnace is the decrease in the quantity of magnetite fed to the smelting unit; otherwise, magnetite tends to build up as solid accretions in the cooler parts of the furnace, thus diminishing the available smelting volume. It should be noted that in copper smelting, "magnetite" refers to any of several compounds such as magnetite, chrome spinels, and olivines which behave similarly.

(2) Cooling Rate

It is important to cool the slag as slowly as possible, usually over a period of several days. The advantages of this practice are as follows:

- The solubility of copper (metallic or as sulfide) decreases with decreasing temperature. Slag quenching would keep copper in metastable solution, whereas slow cooling favors the precipitation of copper sulfides and metallic copper as larger, discrete particles.
- Slow cooling gives more time for surface tension forces to promote coalescence of entrapped and newly precipitated copper-bearing microscopic droplets.

The optimum temperature for these two diffusion-related phenomena to be most effectively enhanced is just below the slag freezing temperature. Slow cooling can typically decrease the copper content of the tailing by a factor of two. In addition, slow cooling promotes the crystallization of fayalite as prisms of 100-200 microns with ferrite particle intergrowth of 10-80 microns. This configuration is easier to crush than quenched amorphous slag.

(3) Process Description

After the slow cooling stage, the slag is crushed and ground and copper is recovered via froth flotation. This process is very similar to ore crushing and flotation. In fact, a mill built for one purpose can easily be modified to serve the other. However, due to differences in specific gravity, grindability, precious metals recovery, copper content, etc., ore and slag cannot be simultaneously fed to the same circuit. A schematic diagram of such a circuit appears in Figure IV-20.

After crushing, the slag is ground, usually to a range of -270 to -325 mesh. Although a few smelters like Harjavalta have been successful in achieving autogenous grinding, most others use steel or cast iron balls for grinding. The consumption of grinding media is an important cost factor, as it is difficult to go below 8 lb of steel/ton of slag milled.

The flotation circuit is rather simple, as only one concentrate is to be separated. Sodium amyl xanthate, sodium isopropyl xanthate, or other alkali xanthates are used as a collector at an approximate rate of 270-300 g/metric ton. A frothing agent is then added (Dowfroth 250 or an equivalent) and the cell overflow is pumped to a thickener from which the thickened concentrate slurry is fed to a disc filter. The moisture in the filtered concentrate is fairly high, due to its fineness. At Harjavalta the slag concentrate contains 13% water. The concentrate is then fed back to the smelter, usually mixed with ore concentrate, flue dust, etc.

(4) Efficiency of the Process

Table IV-35 summarizes the efficiency of slag flotation for selected commercial operations.

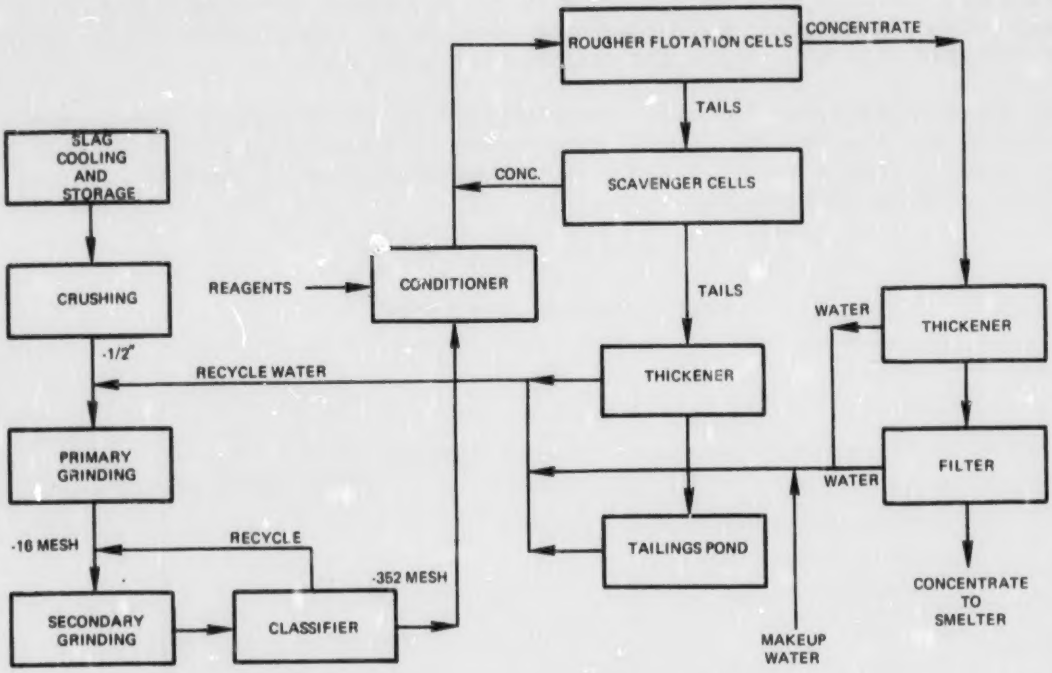

ROUGHER FLOTATION CELLS
CONCENTRATE
TAILS
SLAG COOLING AND STORAGE
CONC.
SCAVENGER CELLS
CRUSHING
REAGENTS
CONDITIONER
TAILS
WATER
THICKENER
-1/2"
RECYCLE WATER
THICKENER
PRIMARY GRINDING
FILTER
WATER
-16 MESH
RECYCLE
TAILINGS POND
-352 MESH
CONCENTRATE TO SMELTER
SECONDARY GRINDING
CLASSIFIER
MAKEUP WATER

Figure IV-20. Typical Slag Milling Flowsheet

TABLE IV-35

EFFICIENCY OF METALS RECOVERY FROM SLAGS BY FLOTATION

	NORANDA	NIPPON MINING		MITSUBISHI	OUTOKUMPU	CANANEA
	Continuous Process	HITACHI	SAGANOSEKI	NAOSHIMA	HARJAVALTA	CONVERTER SLAG
Cu	97	92.7	91.6	93.4	90.1	95.3
Ag	93	93.7	89.2	97.3		94.8
Au	95	94.8	93.6	100.0		
Pt						
As	32					
Sb	29					
Bi	23					
Fe	11					21.7
Si						16.14
S	94					
Pb	16			56.7		
Zn	11			12.4		
Cd	22					
Se	73					
Te	58					
Ni	11					
Sn	17					
Co						

Note: This table shows only the data released by the respective companies. Blanks indicate that data are not available.

Copper and precious metals are recovered from slag with over 90% efficiency. Sulfur is also recovered in the concentrate. Elements that remain with the slag are oxides such as iron, lead, zinc, nickel, etc. These are combined with silica and are discarded as tailings.

The overall importance and wide diversity of the secondary copper stream coming to and leaving the flotation operation is illustrated in Table IV-36. The range is from a low of 4.4% for a conventional plant in Naoshima to over 50% with the Noranda reactor.

TABLE IV-36

SLAG FLOTATION OPERATIONS

	Noranda Continuous Process Making Copper	Naoshima	Harjavalta	
Copper in slag (%)	12(1)	3(2)	2(3)	6(2)
Copper in slag concentrate (%)	50	23	12.2	35
Copper in tailings (w%)	0.5	0.32	0.36	0.52
Percentage of the copper in smelter feed lost in tailings	1.66	negligible	0.27	0.42
Percentage of copper in smelter feed entrained in slag before treatment	51	4.4	1.7	5.6

NOTES: (1) Reactor slag
(2) Converter slag
(3) Flash furnace slag

(5) Treatment of Tailings

The usual treatment for the tailings is to pump them into a lined tailings pond near the plant. The clear water is reused together with the overflow of the thickener, the filter water, and the water from the vacuum pumps. The net water consumption is quite small, less than 10% of the circulating water load.

The tailings still contain up to 0.5% copper, and the very fine particle size of this material has led a number of investigators to think that further copper recovery could be achieved by sulfuric acid leaching under aerated conditions. Indeed, such a procedure carried out in the laboratory for 1 hour at pH 3.0 and 70°C was shown to bring down the copper concentration of the tailings from 0.5% to 0.25%. Copper could then be recovered from the liquor by cementation on iron, and the barren solution could be recycled or neutralized with lime. However, such an operation has not been commercialized nor evaluated on a larger scale.

b. Current Status

Nippon Mining Company apparently was first to develop this process in connection with its oxygen converter smelting. It has since been generally adopted by several other Japanese copper smelters. This process is also used for treating slag at flash smelters such as Outokumpu, and Noranda is presently using it to treat the slag from its continuous copper/matte-making unit.

c. Effluents

(1) Air

No air pollution is generated by this process. Since slag return ports are eliminated from the smelting furnace, this reduces air infiltration and simplifies emission controls on reverberatory or other types of smelting furnaces.

(2) Water and Solid Waste Disposal

As noted, the process produces finely ground tailings which are stored in lined ponds. The water from the tailings ponds is recycled as shown in Figure IV-20.

As long as a tailings pond is in use, its surface is water covered and dust emissions are not a problem. After a pond is abandoned, the pond must be covered with dirt and revegetated. For a smelter producing 100,000 ton/yr of copper, an area approximately 475 sq ft and 24 ft deep is required annually. The cost for solid waste disposal is about $1.90/ton of copper produced.

3. Slag Cleaning in Electric Furnaces

a. Concept and Operations

The metallics exist in slag either as entrapped globules of a second phase (matte or copper) or as metals dissolved in the slag. The electric furnace recovers metallic values by counteracting both mechanisms of loss into the slag:

- By keeping the slag molten and fluid at 2190-2370°F for an extended period of time, it allows for small dispersed entrapped particles to coalesce, settle, and form a matte pool at the bottom of the furnace.

- By providing a reducing environment, it decreases the solubility of copper and other easily oxidizable elements in the slag. To maximize this effect, coal can be added to the bath to supplement the action of the carbon already present in the electrodes. Also, pyrite is usually added to match the sulfur requirement of the metals going from oxides in the slag to sulfides in the matte and reduce the oxygen potential of the slag.

After sufficient retention time has elapsed, the matte phase is tapped and sent to the converter together with the matte coming directly from the smelting furnace. Because of the pyrite additions, the grade of the cleaning furnace matte is somewhat lowered. Typically, if a 50-60% Cu matte is produced in the smelting unit, a 20-40% Cu matte will come out of the electric furnace. The slag tapped from the electric furnace is discarded. A common practice is to granulate and then landfill it.

The fumes of the furnace are collected in bag houses or electrostatic precipitators and recycled to the smelting unit unless they are high in impurities.

The electric furnace can be operated either as a resistance furnace or an arc furnace. The latter mode of operation increases power consumption by almost a factor of two but also increases copper recovery.

The overall copper recovery from slag by electric furnace is comparable to or slightly below that achieved by slag flotation. Typically, a power usage or 100-200 kWh/ton leads to a discard slag containing 0.3-0.5% copper. Precious metals (silver, gold, etc.) are recovered almost entirely in the matte phase. Metals with a high vapor pressure such as zinc and cadmium are volatilized and recovered in the dust as oxides. Bismuth, antimony, and lead tend to volatilize as sulfides. Nickel, cobalt, tin, and lead are consistently recovered in excess of 50% of that in the matte phase.

b. Current Status

Electric slag cleaning has been used in Finland, Sweden, and Japan. At Harjavalta, Outokumpu has retained electric furnace slag cleaning for its nickel plant and is using flotation in the copper plant. In many smelters, both electric furnace and flotation are used for slag cleaning. The slag from the smelting unit is directed to the electric furnace. The converter slag may be recycled to the smelting unit or treated via flotation.

Other ways to use electric arc furnaces to clean slags have been envisioned. The most recent development in this direction is the Mitsubishi process, where both matte and slag flow from the smelting unit to an electric arc settler. (See discussion of the Mitsubishi process.)

c. Effluents

(1) Air

The fumes coming off the furnace must be collected, and the dusts are further processed for recovery of metallic values (zinc, cadmium, etc.). The volume of cleaned gas is insignificant and can be merged with the tail gas of the acid plant prior to venting or mixed with the feed gas to the acid plant.

(2) Water and Solid Waste Disposal

The slag from the electric furnace can be disposed of via dumping in the molten state or dumping after granulation. Since the slag is similar in all respects to reverb slag, disposal is identical to that in the base case and has already been discussed in Section B.

4. Economic Factors

In this section, both slag flotation and electric cleaning are discussed together.

a. Capital and Operating Costs

Based on data in the literature, it appears that a 600 ton/day slag flotation mill would cost about $4.2 million. This would include facilities for slow cooling of the slag.

Table IV-37 shows capital and operating costs for both slag flotation and electric furnace cleaning (resistance furnace operation). The costs are shown on the basis of tons of slag into the plant because this is the critical parameter that determines plant size and operating costs. Because copper contents of the slag can vary widely, it is inappropriate to normalize these costs on the basis of copper recovered. As a rough estimate, the cost of recovered copper is 10-18¢/lb. In slag flotation, the amount of copper in the slag has little influence on the residual copper in the tailings where fineness of grind is the important factor. The optimum grind is achieved when the incremental copper recovery achieved by additional grinding balances the marginal cost of grinding. In many cases, the optimum grind is about 90% in the -270 to -325 mesh range.

Table IV-37 also presents capital and operating costs for electric furnace cleaning. An electric furnace is less expensive, about $2 million for a 600 ton/day furnace. Also, land and building requirements favor the electric furnace over the flotation route. As the slag volume increases and several electric furnaces are needed, these cost differences become less divergent.

Table IV-37 shows that the slag milling process is more expensive than electric furnace cleaning. However, it usually allows recovery of a sufficient amount of extra copper to pay for the higher processing cost. For example, if the electric furnace discard slag is 0.4-0.6% Cu and mill tailings are 0.3% Cu, the incremental copper recovery in a 600 ton/day mill is 0.6-8.1 tons, equivalent to about $720-2200/day. The difference in operating cost is about $700, which balances the incremental recovery. The above suggests that each slag flotation scheme has to be tailored to the specific operation and optimized.

H. THE ARBITER PROCESS

Since the Arbiter process is the only hydrometallurgical process selected for detailed analysis, we have included in this section several general comments that would apply to most hydrometallurgical processes for sulfide concentrates.

1. Concept and Operations

The basic process consists of five separate stages for treatment of copper concentrates. A block flow diagram of the process is shown in Figure IV-21. In the first stage, the copper concentrate slurry is leached with ammonia and oxygen in two parallel trains of reactors. Each of the reactors is well mixed

TABLE IV-37

OPERATING COSTS: SLAG CLEANING PROCESS
(Basis: 600 tons/day of Slag)

			Electric Furnace		Slag Flotation	
	Unit	$/Unit	Units/ Ton	$/Ton Slag	Units/ Ton	$/Ton Slag
CAPITAL INVESTMENT (CI)			$2,000,00		$4,200,000	
OPERATING COSTS						
VARIABLE COSTS						
Grinding Media	lb	0.30	---	---	5	1.50
Electrodes	ton	300	0.0038	1.14	--	--
Electricity	kWh	0.0021	100	2.10	75	1.58
Water	10^3 gal	0.20	---	---	--	0.08
Direct Operating & Maintenance Labor (L)	Man-hr	5.75	0.31	1.78	0.2	1.15
Supervision	15% L		---	0.27	--	0.17
Maintenance Supplies	4% CI		---	0.38	--	0.80
Labor Overhead	35% L		---	0.72	--	0.46
TOTAL VARIABLE				6.39		5.74
FIXED COSTS						
Plant Overhead	65% L			1.33		0.86
Local Taxes & Insurance	2% CI			0.19		0.40
Depreciation	7% CI			0.66		1.40
Capital Recovery	20% CI			1.90		4.00
TOTAL FIXED				4.08		6.66
TOTAL				10.47		12.40

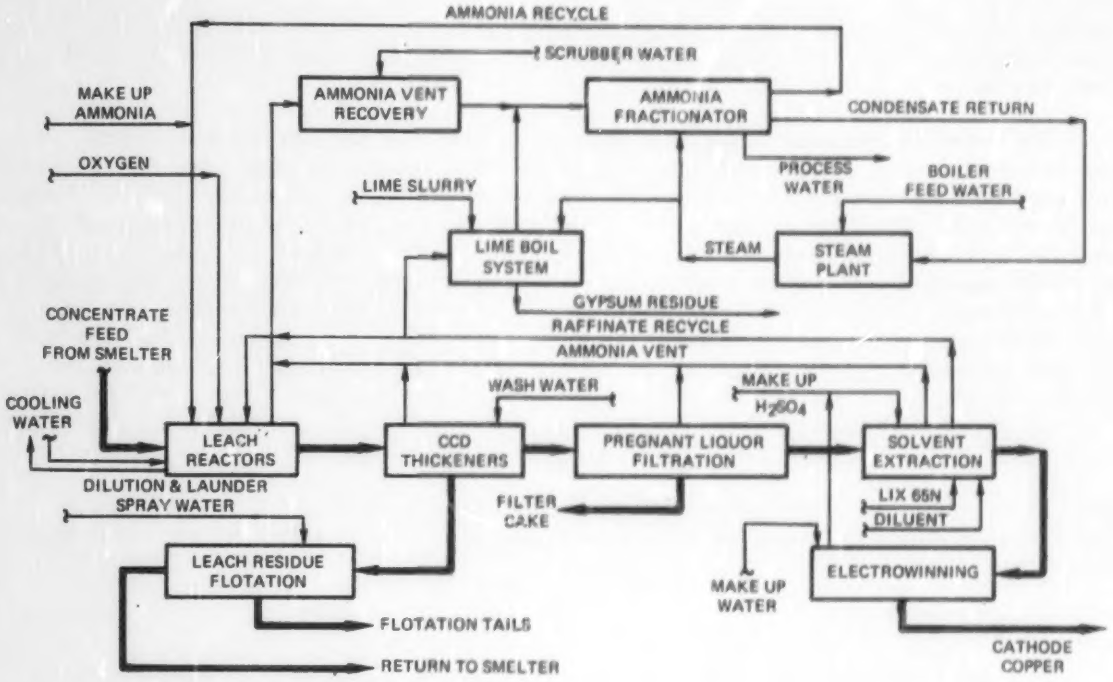

AMMONIA RECYCLE
SCRUBBER WATER
MAKE UP AMMONIA
AMMONIA VENT RECOVERY
AMMONIA FRACTIONATOR
CONDENSATE RETURN
OXYGEN
PROCESS WATER
BOILER FEED WATER
LIME SLURRY
LIME BOIL SYSTEM
STEAM
STEAM PLANT
GYPSUM RESIDUE
CONCENTRATE FEED FROM SMELTER
RAFFINATE RECYCLE
AMMONIA VENT
WASH WATER
MAKE UP H2SO4
COOLING WATER
LEACH REACTORS
CCD THICKENERS
PREGNANT LIQUOR FILTRATION
SOLVENT EXTRACTION
DILUTION & LAUNDER SPRAY WATER
FILTER CAKE
LIX 65N
DILUENT
LEACH RESIDUE FLOTATION
MAKE UP WATER
ELECTROWINNING
FLOTATION TAILS
RETURN TO SMELTER
CATHODE COPPER

Figure IV-21. Anaconda Arbiter Plant - Block Flow Diagram

using the mechanisms from a froth flotation machine which aerates the pulp and increases the dissolution rate. The reaction in this stage is:

$$CuFeS_2 + 4.25\ O_2 + 4\ NH_3 + H_2O = Cu(NH_3)_4^{++} + 0.5\ Fe_2O_3 + 2SO_4^{=} + 2\ H^+$$

The leached residue and pregnant solution are discharged from the leach tanks to a series of countercurrent decantation (CCD) thickeners. The purpose of the CCD section is to separate the pregnant solution from the leached solids. Wash water is added countercurrent to the flow of solids. The pregnant solution from the first CCD thickener is filtered in pressure filters while the washed residue from the last thickener is pumped to a froth flotation section for the recovery of unleached metal values. The concentrate from the flotation section is pumped to the smelter for treatment. At Anaconda this stream contains about 20% of the copper in the initial concentrate and most of its precious metal values.

The clarified pregnant solution from the pressure filtration stage is pumped to the fourth stage of the process, solvent extraction. During solvent extraction, the pregnant solution is contacted with an organic reagent (General Mills LIX 65N reagent) which selectively extracts copper from these solutions. The loaded organic is washed to remove any entrained ammonia and is then fed to the stripping side of the circuit where the copper-loaded organic is stripped with spent electrolyte from electrowinning. The stripped organic is returned to the extraction side of the circuit. The loaded electrolyte is taken to a conventional electrowinning stage where copper in the electrolyte is plated on starter sheets of pure copper to produce copper cathodes according to the reaction $C_u^{++} + H_2O = Cu^o + 2H^+ + 1/2\ O_2$. Insoluble anodes of antimonial lead are used.

The ammonia recovery system regenerates ammonia for use in the leach. The inputs to this system are the raffinate (the barren stream from the liquid ion exchange system containing mainly ammonium sulfate) and exhaust gases from the reactors, thickeners, and solvent extraction stages. Those streams which contain ammonia compounds (mainly the raffinate) are treated in lime boil pots to yield ammonia and calcium sulfate. The ammonia is stripped from the solution by steam flowing countercurrent to the slurry. The slurry from the last lime boil pot is pumped to tailing storage while the stripped ammonia (and the streams containing free ammonia) go to the ammonia fractionator column. The fractionating system contains a fractionator, reboiler, condenser, reflux drum, storage tanks and pumps. Vent gases from other parts of the plant are scrubbed with water which is then fed to the ammonia fractionator.

The plant typically also includes auxiliary facilities such as a boiler plant for making steam and an air separation plant for making oxygen used in the leaching process.

2. Current Status

The Anaconda Arbiter plant is the first large hydrometallurgical process to be placed in commercial operation in the United States for the hydrometallurgical extraction of copper from sulfide concentrates. This plant, located in Montana, was built in 1973-1974 and has a capacity of 36,000 ton/yr of cathodes. It was undergoing initial shakedown operations when the plant was mothballed because of the low price of copper and the absence of feed materials. We understand that the plant is also undergoing some modifications.

The concentrate used in Montana contains primarily chalcocite (Cu_2S) which is leached much more rapidly than chalcopyrite, the more abundant mineral used as a basis for this study. Thus, the specific concentrate used in Montana offers the following advantages:

- The chalcocite can be leached rapidly, requiring smaller leach reactors.
- Because the precious metals are concentrated in the mineral enargite (Cu_3AsS_4), which leaches slowly, the leach is conducted only to dissolve approximately 80% of the copper. The solids from the leaching step are treated by froth flotation to recover the remaining copper sulfide minerals which are then smelted in a conventional smelter. This enables an overall high recovery of copper (about 95-98%) as well as precious metals.
- Because of the overall high copper-to-sulfur ratio in the leachable fraction of the concentrate, the lime requirements in the ammonia recovery section are much smaller than they would be for a standard chalcopyrite concentrate.
- The concentrate is also free of several troublesome trace impurities.

In contrast to the above, chalcopyrite concentrate would require much longer leach times, would require much higher copper recoveries in the leach step, and would require a means for recovering precious metals if present in the ferric oxide sludge, and a means for handling impurities. For the widest applicability of this process, it might be desirable for the process not to rely only on an adjacent smelter.

3. Effluents

Figure IV-22 shows the emission sources while Table IV-38 shows major constituents of effluent streams from the Arbiter process by air, water, and solid waste categories.

a. Air Pollution

The Arbiter process, like most hydrometallurgical processes, causes little direct air pollution. The major emissions from the process are associated with the ammonia recovery system, which would contain traces of ammonia and fugitive emissions of sulfuric acid mist from the electrowinning tank house.

The process is energy-intensive and uses mainly electricity and steam. Some pollution would be associated with the boiler plant in both cases.

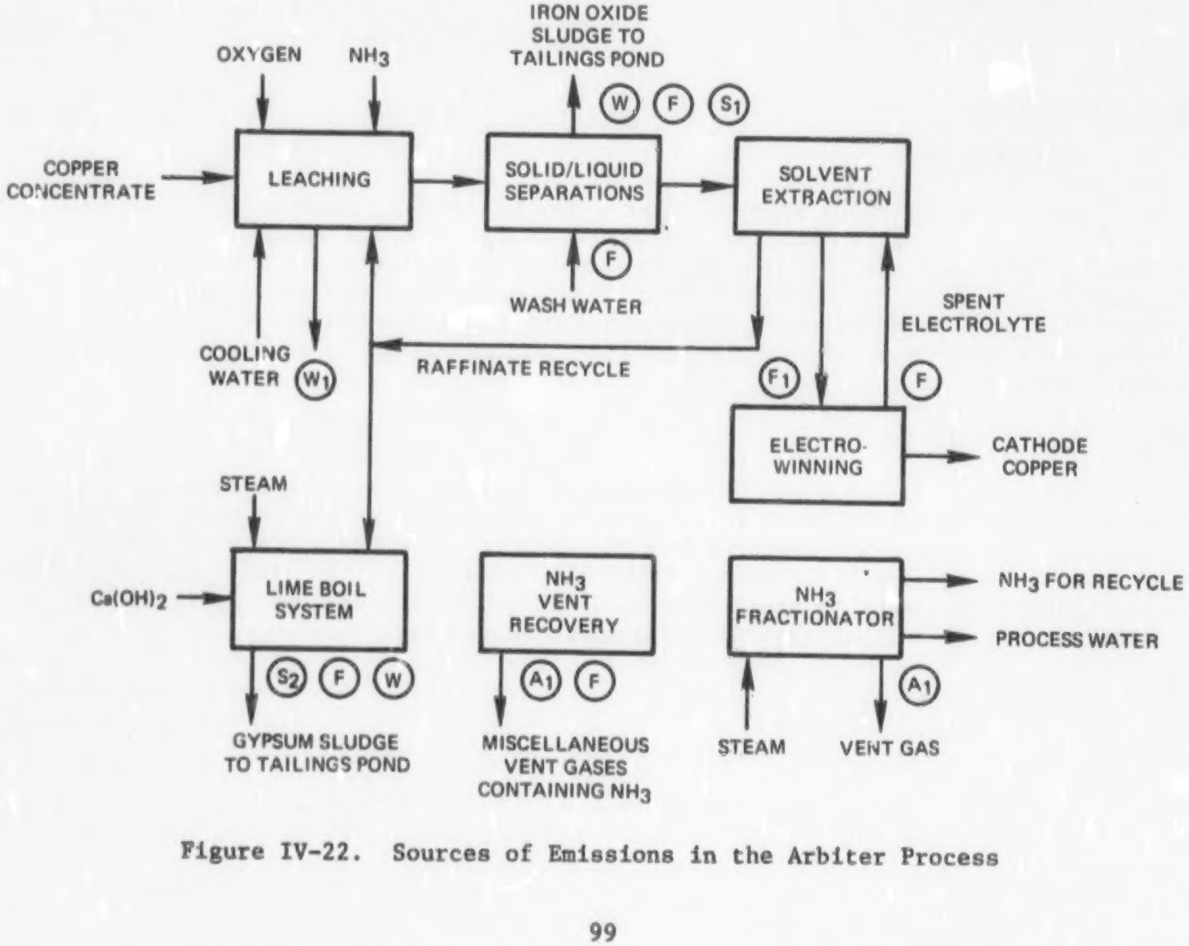

IRON OXIDE SLUDGE TO TAILINGS POND
OXYGEN
NH3
W
F
S1
COPPER CONCENTRATE
LEACHING
SOLID/LIQUID SEPARATIONS
SOLVENT EXTRACTION
F
WASH WATER
SPENT ELECTROLYTE
COOLING WATER
W1
RAFFINATE RECYCLE
F1
F
ELECTRO-WINNING
CATHODE COPPER
STEAM
Ca(OH)2
LIME BOIL SYSTEM
NH3 VENT RECOVERY
NH3 FRACTIONATOR
NH3 FOR RECYCLE
PROCESS WATER
S2
F
W
A1
F
A1
GYPSUM SLUDGE TO TAILINGS POND
MISCELLANEOUS VENT GASES CONTAINING NH3
STEAM
VENT GAS

Figure IV-22. Sources of Emissions in the Arbiter Process

TABLE IV-38

EMISSIONS FROM THE ARBITER PROCESS

Stream	Stream Size	Major Constituents
• Air Pollution and Fugitives		
A-1 - NH_3 Vent Recovery System and Fractionator	10,000-50,000 scfm (Est.)	Traces of NH_3
F-1 - Tank House Air	NA*	H_2SO_4 Acid Mist
• Water Pollution		
W-1 - Cooling Water Blowdown	NA*	Chlorides
• Solid Wastes		
S-1 - Leach Residue	1.3 dry ton/ton of copper	Iron oxide, insoluble minerals such as silica, pyrites, bismuth sulfides, lead, arsenic and precious metals, if present
S-2 - Gypsum Sludge	4.5 dry ton/ton of copper	Calcium sulfate with traces of arsenic, zinc and other heavy metals

*NA = Not Available

b. Solid Wastes

The two solid waste streams are the calcium sulfate sludge from the ammonia recovery system and the iron oxide sludge from the leach residue. These wastes would require storage in lined ponds with a wet top surface to prevent dust emissions during the period the pond is in use and proper cover after the pond is abandoned. The two sludges would contain impurities if present in the concentrates. The behavior of impurities is discussed in the next section.

c. Water Pollution

The Arbiter process can be operated so that there is no net aqueous discharge to the environment in areas where solar evaporation is high, such as Arizona, the location considered for this study. In areas where evaporation is insufficient or with an excess rainfall, depending on the plant water balance, it might be necessary to bleed some water from the tailings ponds. Treatment necessary would be that typical for comparable waters.

4. Technical Considerations

a. Products

The copper produced by the Arbiter process would be more or less equivalent in quality to other electrowon copper. The sulfur values could either be sold as ammonium sulfate fertilizer when and where market and transportation conditions permit or be discarded as calcium sulfate sludge. In conventional copper processing, the sulfur values are typically converted to sulfuric acid or discharged to the atmosphere. These options are not present for hydrometallurgy. The iron would be discarded as an iron hydroxide sludge. In all probability, this sludge would be too impure to be considered as a feed to iron and steel making. The major unknowns in the Arbiter process relate to its ability to recover the precious metals from the iron oxide sludge by cyanidation (dissolving precious metals in a solution of cyanide ions) and to the behavior of trace metal impurities that are always present in the concentrates.

b. Impurities

Only limited data are available on the behavior of impurities during processing. Available information indicates the following:

- Arsenic - When the concentrates are high in iron, the arsenic is precipitated as ferric arsenate. With concentrates low in iron the arsenic is precipitated as calcium arsenate during the lime boil. In the former case, arsenic would be present in the leach residue and in the latter case, it would be present in the gypsum sludge, both of which are ultimately disposed of to the land.

- Cobalt and Nickel - These metals would be expected to dissolve in the leach solution and build up in it unless they are removed by precipitation or by ion exchange.

- Selenium and Tellurium - Nothing is known at the present time. They may remain in the leach residue.

- Lead - Lead would be oxidized to lead sulfate or basic sulfate and remain in the leach residue.

- Zinc - Zinc is removed during the lime boil either as a hydroxide or basic sulfate. Alternatively, zinc can be recovered by solvent extraction/electrowinning, if present in concentrations such that this incremental processing is economically justified.

- Precious Metals - Precious metals can be recovered in two ways. At Anaconda's plant operations, only 80% of the copper will be leached. This leachable fraction, chalcocite (Cu_2S), is low in precious metals. A slowly dissolving fraction, enargite (Cu_3AsS_4), contains most of the precious metals. Thus, it is possible to recover the unleached sulfides by a simple froth flotation step and treatment of this flotation concentrate in the conventional manner in the existing smelter. In general, it appears that when copper extractions exceed 97%, the silver and gold recoveries by flotation are very low (under 25%). The silver and gold, however, can be recovered by cyanide leaching of the residues. Alternatives would be brine (NaCl) leaching. Anaconda claims that high silver and gold extractions have been observed when "cyaniding" such residues and that cyanide losses are related to the amount of copper remaining in the residues rather than to the presence of hydrated ferric oxides. However, no data have been released because Anaconda considers this to be proprietary information.

- Bismuth - Bismuth, present as bismuthinite, is converted either to a heavily oxidized colloidal precipitate or to a sulfide with oxidized surfaces during the ammonia leaching process. In either case, this bismuth is not floated during subsequent flotation of the leach residue and reports to the leach tailings fraction.

c. Scrap

The process should be able to handle copper scrap as long as its particle size permits. The leaching of copper scrap in similar solutions has been practiced on a commercial scale and presents no obvious technical or environmental problems.

5. Economic Factors

a. Basis for Comparison

The hydrometallurgical processes produce cathode copper usually equivalent in quality to electrorefined cathode copper. Thus, they have to be compared with conventional smelting plus refining. These processes claim the following advantages (some of them still unproven):

- They have a much smaller minimum economic size. The smallest economic size for a conventional smelter is at least 100,000 ton/yr. It is even larger for an electrolytic refinery. A hydrometallurgical plant could be viable in the range of 20,000-40,000 ton/yr of copper.

- The capital investment per unit of output is about the same. Large smelters and refineries cost about \$1200/annual ton. The smaller hydrometallurgical plants would cost about \$1000-1200/annual ton.

- The hydrometallurgical processes are truly continuous processes as opposed to the batch/continuous processing inherent in conventional pyrometallurgical processing. This means that the hydrometallurgical processes can be designed to have a significantly lower labor component compared with the base line pyrometallurgical route.

- In a hydrometallurgical plant, the sulfur in the concentrate is converted to forms other than sulfuric acid, such as $(NH_4)_2SO_4$, or $CaSO_4$ sludge. This is advantageous in locations where air pollution regulations are very stringent.

All the above suggests that the applications of these processes are likely to be in locations where sulfuric acid markets are non-existent and where the construction of a full-sized smelter represents an undue economic risk because the growth in copper demand is sluggish. Because of this it would not be proper to compare a smaller-sized Arbiter plant with a conventional smelter-refinery complex sized at 100,000 ton/yr.

A comparison with conventional technology is feasible when custom smelting is taken into account. A custom smelter offers smelting and refining services to producers of concentrates from several sources. It is able to achieve economies of scale by pooling of concentrates. Typical custom smelting and refining charges at the present time using conventional technology would be about 18¢/lb copper. A comparison of this figure with those in Tables IV-6 and IV-8 shows that the custom smelting and refining charge is less than the cost of smelting and refining in a new installation. This is because existing custom smelters and refineries are old and have lower fixed costs while inflation has substantially increased the capital investment requirements for new facilities.

Another problem specific to the comparison of the Arbiter process with the base line is related to the fact that the initial application of the Arbiter process is not to the usual chalcopyrite concentrate but to a chalcocite-enargite concentrate.

Nevertheless, for our comparison, we have used a clean chalcopyrite concentrate as a basis because this is the most abundant copper concentrate in the United States and in the world. This choice makes the comparison less favorable for the Arbiter process because of the higher sulfur content, longer leach times, and higher lime requirements for neutralization. Consistent with industry practice and the base case, credit for precious metals and/or impurities has been ignored. However, it appears that with the Arbiter process, the incremental costs of treating leach residues for precious metal recovery would be higher than the incremental cost of recovering the same metals in conventional processing from anode mud residue.

Finally, it should be noted that a comparison of conventional smelting and refining versus the Arbiter process cannot be made at constant or equivalent emissions to the environment but rather can be made on the basis of both processes meeting currently acceptable environmental standards (e.g., BATEA, BPCTCA and NSPS).

b. Capital and Operating Costs

Table IV-39 shows estimates of capital and operating costs for the Arbiter process based on chalcopyrite concentrates.

c. Comparison with Conventional Technology

(1) Energy Use

Energy used for this process (mainly electricity and steam) amounts to about 56 x 10^6 Btu/ton (fossil fuel equivalent) according to Arbiter (1974).

TABLE IV-39

OPERATING COSTS: THE ARBITER PROCESS
(Basis: Chalcopyrite concentrates 36,000 ton/yr of copper)

	Unit	\$/Unit	Units/Ton	\$/Ton Cu
CAPITAL INVESTMENT (CI)	\$/annual ton		\$1000	
OPERATING COSTS				
VARIABLE COSTS				
Ammonia	ton	150.00	0.15	22.50
Oxygen	ton	15.00	2.5	37.50
CaO	ton	25.00	2.3	57.50
LIX and Organic	gal	4.00	3.4	13.60
Miscellaneous Chemicals	---	---	---	15.00
Purchased Steam (from Fuel Oil)	10^3 lb	3.06	20.00	61.20
Purchased Electricity	kWh	0.021	3000.00	63.00
Water: Process	10^3 gal	0.20	1.6	0.32
Cooling	10^3 gal	0.05	10.0	0.50
Direct Operating and Maintenance Labor (L)	Man-hr	5.75	7.00	40.45
Supervision (S)	L	15% L	---	6.04
Maintenance Materials	CI	4% CI	---	40.00
Labor Overhead	L+S	35% (L+S)	---	16.27
TOTAL VARIABLE COSTS				373.88
FIXED COSTS				
Plant Overhead	L+S	65% (L+S)	---	26.65
Local Taxes & Insurance	CI	2% CI	---	15.00
Depreciation	CI	7% CI	---	70.00
Capital Recovery	CI	20% CI	---	150.00
TOTAL FIXED COSTS				261.65
TOTAL COSTS				635.53

On the same basis, he reports 55.4 x 10^6 Btu/ton for conventional processing and 30.4 x 10^6 Btu/ton for flash smelting. Out figures for the pyrometallurgical processes are lower.

The hydrometallurgical processes are inherently less energy efficient than the newer pyrometallurgical processes because in pyrometallurgical operations the heat of oxidation of sulfur and iron is utilized to melt the concentrates. In the Arbiter process, sulfur and iron are oxidized at about 200°F. This heat has to be carried away from the leach reactors using cooling water. This low-grade heat cannot be utilized in the plant and has to be dissipated.

(2) Pollution Aspects

As mentioned earlier, there is considerable alteration in the effluent profile with the Arbiter process compared to the base line. Air pollution is reduced to very low levels. New forms of solid wastes (leach residue and calcium sulfate sludge) are produced. These, along with the associated liquid effluent, would contain several of the trace impurities in the concentrates and would require proper storage. In our calculations, we have assumed storage ponds with water recycle for both tailings. If a water stream has to be bled, we have assumed that the overflow from the calcium sulfate pond could be discharged. Depending upon evaporation/rainfall ratio this discharge might be eliminated.

Since hydrometallurgical processing, by its very nature, takes place in closed containers, the emissions from a plant of this type are at specific points which (at least conceptually) might be easier to control than the emissions from several of the pyrometallurgical operations in conventional smelting. Thus, the hydrometallurgical plant might be in a better position to weather the changing regulations regarding fugitive emissions and trace metal emissions than the conventional plant.

The costs of solid waste disposal are about $33.06/ton of copper as shown in Table IV-40.

(3) Byproducts

For most concentrates it might be economical to treat the iron oxide sludge via cyanidation for precious metal recovery prior to its disposal in ponds. In special situations, it might be possible to sell ammonium sulfate for fertilizer use (assuming that trace impurities can be removed or demonstrated to be non-deleterious, depending on their nature and the crop to which the fertilizer is applied).

(4) Cost Comparison

Table IV-39 shows that direct operating costs are about 18¢/lb and total operating costs are about 32¢/lb. These costs are for chalcopyrite concentrates and, as mentioned earlier, the process economics are more favorable with chalcocite concentrates. These costs are not competitive with custom smelting and refining charges of about 18¢/lb or even smelting and refining costs in a new large smelter and refinery of about 25¢/lb. This

TABLE IV-40

ARBITER PROCESS - SOLID WASTE DISPOSAL
36,000 ton/year of copper

Lined Disposal Sites - covered each year - lined with membrane

Required: 14.5 acre/yr - 10 ft deep

Estimated Yearly Investment (Expenditure) In Site Preparation and Closure	$ 450,000
Estimated Hauling Costs @ $2.00/Wet ton	740,000
Total Estimated Annual Costs	$1,190,000
Unit Costs ($/ton copper)	$ 33.06

would suggest that the Arbiter process (and perhaps hydrometallurgical processes generally) are applicable only for special concentrates, such as the chalcocite concentrates being utilized by Anaconda, in cases where custom smelting capacity is either not available or where the required pyrometallurgical plant is too small to be economical. This would explain why much of the activity in hydrometallurgical process development in the United States has been undertaken by the smaller, non-integrated mining companies such as Cyprus and Duval.

(5) Commercial Considerations

Users of the process would expect to pay a royalty to Anaconda for the process or operate under some sort of licensing agreement. These costs are not included in Table IV-39. It should also be noted that hydrometallurgical processes typically have a smaller inventory of metal in the process compared to smelting. However, because the process operations are more sensitive to concentrate mineralogy, more extensive blending and stockpiling of feed materials might be necessary.

V. IMPLICATIONS OF POTENTIAL PROCESS CHANGES

A. INTRODUCTION

The process changes considered by us for detailed analysis fall into the following four categories:

- New pyrometallurgical processes
- The use of oxygen in smelting
- Metal recovery from slags (electric furnace and flotation)
- Hydrometallurgy (Arbiter process)

In this chapter we discuss the implications of the process changes discussed in Chapter IV grouped into the four categories mentioned above.

B. PYROMETALLURGICAL PROCESSES

Of the process units used in conventional smelting, the reverb has become obsolescent because of high energy costs and because of the need to curb emissions of SO_2 to the atmosphere. The new pyrometallurgical processes use smelting units which produce concentrated SO_2-containing streams. Such streams are suitable for the manufacture of sulfuric acid or for the reduction to elemental sulfur. This makes it possible to increase the degree of sulfur capture from 50-70% with conventional smelting (achieved via control of converter or converter plus roaster gases) to over 90% (achieved via control of both smelting unit and converter gases).

While sulfur capture prevents the emissions of sulfur dioxide to the atmosphere, this captured sulfur has to be utilized or disposed. In the United States, the major copper deposits and the copper mining, beneficiation, and smelting activities are mainly in the West, and are concentrated in particular in the Southwest. These locations are distant from the traditional sulfuric acid market (Florida). The cost of shipping this acid to the traditional markets outside the Southwest is prohibitively expensive; i.e. about \$40/ton of acid for transportation alone versus about \$20-30/ton for acid production. Thus local markets must be found or the acid must be disposed of in an alternate, acceptable fashion. The transportation constraints have resulted in the availabiltiy of low-cost acid in the West. Two trends have developed as a result of the availability of this low-cost acid. The first is the construction of several wet-process phosphoric acid plants based on smelter acid and the lower grade western phosphate rock. The second trend is the increasing use of sulfuric acid to recover copper from such marginal resources as tailings, mine dumps, and oxide ores. Since many of these ores contain high concentrations of acid-consuming materials, this approach not only disposes of the acid by neutralizing it, but also recovers copper at the same time. Because of the arid nature of the Southwest, dumps and surface deposits can be leached without contamination of groundwater. This would not be possible in other regions of the United States. Alternative ways of disposing of the sulfur values as calcium sulfate are also being examined (neutralization of sulfuric acid or direct roasting of concentrates with limestone to fix the sulfur). In the future it is conceivable that sulfuric acid would still be in surplus in the West and that neutralization with limestone would be quite expensive. In that case it might be more economical to construct smelters closer to the traditional acid markets east of the Mississippi and transport the ore concentrates by rail to such locations for smelting.

A few years ago, a custom smelter considered this approach. However, none of the independent mines were willing to participate since smelting charges from the new smelter would have been quite a bit higher than the charges from existing, partially depreciated smelters.

It is possible to convert concentrated SO_2 streams to elemental sulfur instead of converting them to sulfuric acid. Natural gas, light hydrocarbon liquids, or coal can be used, depending on the process selected. The elemental sulfur produced in this fashion can be shipped a longer distance than the corresponding sulfuric acid, or such sulfur can be stored. The cost of producing such sulfur is quite high, exceeding about 5¢/lb of copper contained in the concentrates, versus a pollution control cost of about 3¢/lb of copper when making sulfuric acid. It therefore appears that elemental sulfur would be considered only in cases where all other options are not feasible.

Compared to conventional smelting, the newer smelting processes are quite energy efficient and save from 30 to 50% of the energy over conventional smelting. Since both conventional and newer processes are quite flexible in their use of any form of fossil fuel, there is no additional conservation in form value. The adoption of these new processes not only reduces emissions to the atmosphere but also reduces fuel requirements and the pollution that is generated from the fuel.

The major handicap of the new pyrometallurgical processes is that their ability to handle impure concentrates (concentrates containing As, Sb, Bi, Zn, Pb, Se, Te, etc.) has not been proven. In many cases when impurity concentrations are moderate (say, under 5% total impurities), impurity elimination is possible by making a matte in the new smelting unit and using a batch converting operation to volatilize these impurities. When impurity concentrations are higher, it is necessary to roast the concentrates and to smelt the calcines in these new smelting units. This technology is also unproven.

In general, these new processes are capable of recycling less scrap than with conventional processing. However, several techniques (oxygen enrichment, use of coke in converters, etc.) are available. The use of these techniques can enable the new processes to recycle comparable quantities of scrap.

Pyrometallurgy, in general, offers signficant economies of scale. Thus, another handicap of the new pyrometallurgical processes is that they too need to be constructed at a large size. The smallest economic size is approximately 100,000 ton/yr.

The growth rate in copper consumption in the United States has been 3-4% a a year. Assuming that this growth rate continues and that U.S. metal production is increased to keep up with this (as has been the trend in the past), the United States would require new capacity of about 600,000 ton/yr each year to fulfill these requirements by 1985-1990. We believe that some of this increased production will come from hydrometallurgical operations on oxide and sulfide ores and the number of new pyrometallurgical smelters might be 3-4 at over 100,000 ton/yr each. We believe that these smelters would utilize the newer processes or possibly electric smelting (if favorable power costs can be negotiated or if the impurity content of the concentrates is high).

These new pyrometallurgical processes are economically viable only if the metal contained in the slag is recovered. The slag treatment processes are an integral portion of the new smelting technology and their costs have been included in considering the process economics. Their costs have been estimated separately in Section G for illustrative purposes.

C. OXYGEN USE IN SMELTING

The use of oxygen in smelting decreases fuel requirements and is energy-efficient overall because the decrease in fuel requirements is usually larger than the incremental energy required in the oxygen separation plant. The most beneficial aspect of using oxygen is the ability to increase production significantly from existing units and reducing the capital costs per unit of output from new units. A smaller benefit is the ability to melt more scrap. However, most of the easily available scrap is already recycled, and the marginal scrap is probably mixed copper-iron scrap which is smelted in limited quantities in existing smelters. These advantages would provide the major driving force for the widespread adoption of the use of oxygen enrichment in industry for both existing and new processes.

D. RECOVERY OF METALS FROM SLAG

As mentioned earlier, the availability of these processes has made it possible to use the new smelting technology such as Outokumpu flash smelting. The additional benefits of slag cleaning, with less flux added for control of viscosity and fluidity, are that the total slag volume and flux requirements are decreased. Since converter slag is not recycled to the smelting unit, problems associated with accretions of magnetite are avoided. This makes it possible to operate longer campaigns in the smelting unit without the loss of capacity that occurs when magnetite deposits on the bottom. The elimination of converter slag recycle also gets rid of the converter slag launder which is a major point for air infiltration into the smelting unit. This air infiltration is undesirable because it increases fuel requirements and dilutes the SO_2 in the smelting unit gases.

These processes are also applicable in conventional smelting; for example, converter slag can be treated via slag flotation instead of returning it to the reverb.

E. THE ARBITER PROCESS

The Arbiter process, and hydrometallurgical processes in general, would be adopted mainly in regions distant from sulfuric acid markets and where a full-sized pyrometallurgical smelter is risky. The adoption of hydrometallurgical techniques would depend on the availability of surplus custom smelting capacity in the United States. Overall, we believe that 3-5 small hydrometallurgical plants will be operating in the 1980's, particularly on concentrates with favorable mineralogy. These processes have little or no air pollution, but produce significant quantities of solid waste which are different from the conventional solid waste from the smelter. These wastes can be stored in lined ponds so that they have only a minimal interaction with the environment.

F. SUMMARY

The copper industry can be expected to increase metal production by about 600,000 ton/yr by 1985-1990 if past trends continue. A major portion of this increase will result from the adoption of new pyrometallurgical processes with or without oxygen enrichment but with associated slag cleaning technology. These processes would result in a 30-50% reduction in energy usage per ton of copper. The capital costs for these smelting processes are about $750/annual ton of copper and operating costs would be about 15-17¢/lb copper. This technology would increase sulfur capture from the current level of 50-70% to over 90%.

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APPENDIX A

PRESENT COPPER TECHNOLOGY

1. FEEDSTOCKS

There are seven major copper producing areas in the world: (1) the western United States; (2) the western slope of the Andes in Peru and Chile; (3) the central African Copperbelt in Zambia and Zaire (Kinshasa); (4) the Ural Mountains and the Kazakstan region in the U.S.S.R.; (5) the Precambrian area of central and western Canada; (6) the Keweenaw Peninsula of Northern Michigan; and (7) the Southwest Pacific (Australia, Bougainville).

Of the many copper minerals, only chalcocite, chalcopyrite, bornite, chrysocolla, azurite, and malachite are important commercially. Copper ores occur in many types of deposits in various host rocks. Porphyry copper deposits account for about 90% of the U.S. production and much of the world output, and contain most of the estimated commercial copper reserves of the world.

From a processing viewpoint, copper ores can be classified in three categories: sulfide ores, native copper ores, and oxide ores.

A sulfide ore is a natural mixture containing copper-bearing sulfide minerals, associated metals, and gangue minerals (e.g., pyrites, silicates, aluminates) that at times have considerable value in themselves (e.g., molybdenum, silver, gold, as well as other metals). Most sulfide ores belong to one of three major groups, all of which are represented in the United States, namely:

- The porphyry copper and Northern Rhodesian type deposits that carry copper mostly in the form of chalcocite (Cu_2S), chalcopyrite ($CuFeS_2$) and bornite (Cu_5FeS_4). Copper ranges from a fraction of one percent to several percent, and iron is generally low. The deposits in the southwestern United States are of this type.

- Deposits, such as those found in Rio Tinto in Spain, in Cyprus, and in Tennessee, commonly known as cupriferrous pyrite, which generally have 1-3% copper as chalcopyrite, and contain abundant amounts of pyrite and pyrrhotite. Generally, copper-to-iron ratios and copper-to-sulfur ratios are low.

- Arsenic-bearing copper ores, such as enargite (Cu_3AsS_4), with deposits occurring in Butte, Montana; Yugoslavia; Tsumeb in South West Africa; and the Philippines.

The sulfide ores are treated primarily by crushing, grinding, and froth flotation to produce a concentrate (or several concentrates) of sulfide minerals and reject the worthless gangue as tailings.

Native copper ores are those in which some of the copper occurs as the native metal. The Lake Superior District in Michigan is the only major source of ore of this type. Although the reserves of this ore are quite extensive, it contributes only a small portion of the total U.S. mine production of copper.

All non-sulfide, non-native ores of copper are termed "oxide" ores, the oxide copper content being measured by and synonymous with solubility in dilute sulfuric acid. An oxide copper ore can contain copper oxide, silicate or carbonate minerals and gangue. The oxide ores have been treated metallurgically in a variety of ways, the character of the gangue minerals having a very important bearing on the type of metallurgical treatment used. Oxide ores in the United States are treated primarily by leaching with dilute sulfuric acid.

Commonly associated with copper are minor amounts of gold, silver, lead, and zinc, the recovery of which can improve mine profitability. Molybdenum, lead and zinc are recovered as sulfides by differential flotation. Minor amounts of selenium, tellurium, and precious metals are extracted in electrolytic refining. On the other hand, arsenic, antimony and bismuth in the ores cause problems in standard pyrometallurgical processing and electrorefining, and thus their presence is a cost penalty. Nickel and cobalt can interfere with electrolytic refining, but they do not occur in significant amounts with the U.S. copper deposits.

In 1964, the Bureau of Mines reported domestic reserves of 75 x 10^6 tons of metal in ore averaging 0.86% copper, assuming recovery at 90% of gross metal content. An additional 58 x 10^6 tons of copper was estimated as potential resources recoverable with technological or economic improvements. Arizona, Montana, Utah, New Mexico, and Michigan accounted for more than 90% of the total reserves.

A 1973 study*/estimated the total known domestic resources of copper economically available at various copper prices, allowing for a 12% return on investment:

Price	Resources (10^6 ton)
$2.00/lb	180
0.75/lb	115
0.50/lb	83

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*IC 8598, "Economic Appraisal of the Supply of Copper," U.S.B.M., 1973

The 83 x 10^6 tons of reserves indicated above represent 49 years of supply at our present production rate of about 1.7 x 10^6 ton/yr.

A comparison of U.S. copper resources with those of the rest of the world (see Table A-1) indicates that the United States has about 20% of the world's copper resources. It is also evident, however, that many areas of the world have significant copper resources. The major resources are in South America, Africa, U.S.S.R., Canada, Mexico, and Europe.

2. PROCESSING

a. Mining

About 85% of the total copper ore mined comes from open pits; the rest comes from underground mines. Underground mining methods for copper ores involve caving and/or cut-and-fill mining.

b. Beneficiation

The different mineral forms (sulfides, carbonates, oxides, native copper, etc.) require different processing techniques. Many methods have been used to beneficiate the ores; generally only the sulfide ores are amenable to concentration procedures such as grinding and froth flotation.

TABLE A-1

IDENTIFIED AND HYPOTHETICAL COPPER RESOURCES
(10^6 Tons)

Area	Identified[1]	Hypothetical[2]
United States:		
Eastern	10	5
Western, except Alaska	64	75
Alaska	2	20
Canada	19	50
Mexico	18	20
Central America	1	6
Antilles	2	1
South America	80	50
Europe, excluding U.S.S.R.	25	20
Africa	53	50
U.S.S.R.	39	50
Middle East - South Asia	4	20
China	3	?
Oceania, including Japan	21	30
Australia	3	3
Total	344	400

1. Identified resources: Specific, identified mineral deposits that may not be evaluated as to extent and grade and whose contained minerals may or may not be profitably recoverable with existing technology and economic conditions. Based on all categories of reserve figures plus estimates where no figures are available. Amounts are tentative and accuracy will be refined in subsequent publications.

2. Hypothetical resources: Undiscovered mineral deposits, whether of recoverable or subeconomic grade, that are geologically predictable as existing in known districts. Based generally on indentified resource figures times a factor assigned according to geologic favorability of the region, extent of geologic mapping, and exploration.

Source: Geological Survey professional paper 820, "United States Mineral Resources," Brobst and Pratt, 1973.

(1) Sulfide Ores

These ores, the most important source of copper, are concentrated by froth flotation. This procedure requires crushing and grinding and classification to about 100 mesh or finer to liberate the particles. Grinding is usually the largest cost item in the process. After grinding, the ore-water mixture is treated with reagents to condition the sulfide particles so that their surfaces become air-avid. The sulfides are then collected with the froth produced in the flotation cells. The final concentrate may contain 11% to 32% copper. Typically flotation is used to separate copper sulfides from pyrite, recover molybdenum from copper concentrate, and recover copper concentrate from complex lead-zinc-copper ore. A typical flowsheet for flotation of a sulfide ore is shown in Figure A-1.

(2) Oxide Ores

Oxide ores occurring in the United States are generally not amenable to flotation, but are generally soluble in various leaching solutions.

Acid Leaching

The ore is properly sized, if necessary, and leached with acid, which dissolves the copper. Depending on ore grade and characteristics, the ore is leached in vats (by percolation or with agitation), in heaps, or in place.

Sulfuric acid is the usual solvent for oxidized copper minerals. The presence of ferric sulfate in the leach solution can solubilize some sulfide minerals such as chalcocite. For dissolution of the oxide minerals, about 1.5 lb of acid/lb of contained copper is required, but total consumption of acid is often much greater because of reaction with gangue minerals.

Copper is recovered from dilute leach solutions by precipitation with scrap iron, and from concentrated leach solutions by electrowinning.

Other minor methods include ammonia leaching, cyanide leaching, the segregation process, and oxide ore flotation.

(3) Mixed Ores

The treatment of mixed ore, that is, ore containing both sulfide and oxide minerals, depends on the proportions of the two types of minerals. If sulfides predominate, flotation is used, with reagents that favor flotation of oxide minerals. When the ore contains almost equal amounts of sulfide and oxide minerals, combinations of leaching and flotation are used.

c. Smelting

Because most of the U.S. copper is extracted from low-grade sulfide ores that require concentration, current pyrometallurgical practice for recovery of copper from its sulfide concentrates is fairly uniform from smelter to smelter and is adapted to treating fine grained sulfide concentrates consisting mainly of copper and iron sulfides and gangue.

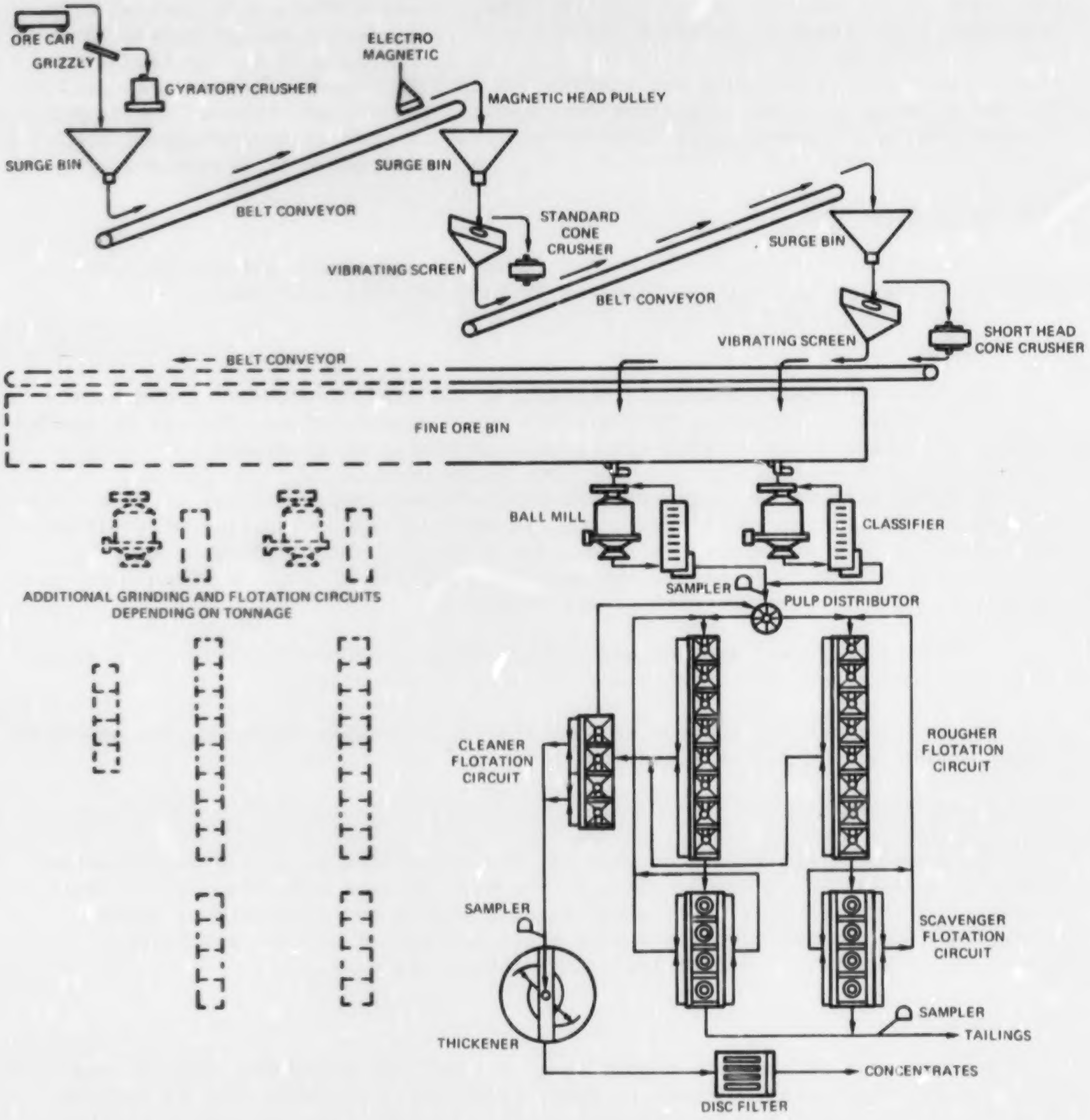
ORE CAR
GRIZZLY
GYRATORY CRUSHER
ELECTRO MAGNETIC
MAGNETIC HEAD PULLEY
SURGE BIN
SURGE BIN
BELT CONVEYOR
STANDARD CONE CRUSHER
VIBRATING SCREEN
SURGE BIN
BELT CONVEYOR
SHORT HEAD CONE CRUSHER
VIBRATING SCREEN
BELT CONVEYOR
FINE ORE BIN
BALL MILL
CLASSIFIER
ADDITIONAL GRINDING AND FLOTATION CIRCUITS DEPENDING ON TONNAGE
SAMPLER
PULP DISTRIBUTOR
CLEANER FLOTATION CIRCUIT
ROUGHER FLOTATION CIRCUIT
SAMPLER
SCAVENGER FLOTATION CIRCUIT
SAMPLER
TAILINGS
THICKENER
CONCENTRATES
DISC FILTER

Figure A-1. Typical Flowsheet - Sulfide Copper Ore Flotation

Copper's strong affinity for sulfur and its weak affinity for oxygen as compared with that of iron and other base metals in the ore forms the basis for the three major steps in producing copper metal from sulfide concentrates; roasting, smelting and converting.

(1) Raw Materials

Flotation concentrates containing from 15-30% copper constitute the bulk of the feed to the smelters. In addition, smelters will charge cement copper (produced by acid leaching of oxide ores and precipitation with iron) containing 70-85% copper, siliceous flux and limestone and a quantity of direct smelting ore containing 4-8% copper. This type of ore, when available, functions as a source of copper as well as a flux.

(2) Drying

The flotation concentrates received by the smelter are in the form of a wet filter cake and can contain 10-15% moisture. Cement copper can contain as much as 30% moisture. The charge to a reverberatory furnace can be dried so that its overall moisture content is 4-8% without unduly increasing dusting problems in the reverb. The removal of moisture in drying reduces the fuel requirements in the reverb. Also, the drier acts as a blender for homogenizing the charge. Rotary or multiple hearth driers are used for drying the feed materials.

(3) Roasting

About half the copper smelters in the United States roast their charge prior to feeding in the reverberatory furnace. The older smelters use multiple hearth roasters for this purpose while the new smelters use fluidized bed roasters.

The object of roasting copper sulfide ores and concentrates is to regulate the amount of sulfur so that the material can be efficiently melted and to remove certain volatile impurities such as antimony, arsenic, and bismuth. However, in modern practice, the grade of the concentrate produced from some sulfide ores is sufficiently controlled at the concentrator to eliminate roasting prior to reverberatory smelting. In the case of custom or toll smelters, the composition of feed materials can vary widely. Hence, roasting is practiced to blend and control the sulfur content of the charge.

Elimination of some of the sulfur in roasting results in a higher grade matte in the reverberatory furnace and hence decreases the oxidizing load on the converters. Sulfide roasting is autogeneous and additional fuel is not required. The charging of hot roasted calcines into the reverberatory furnace can decrease its fuel consumption per ton of charge by about 40% and consequently increase reverb capacity. In addition, roasting also reduces the emissions of sulfur dioxide from the reverb. The reason for this is as follows: the two major constituents of concentrates utilized by almost all the U.S. smelters are chalcopyrite ($CuFeS_2$) and pyrite (FeS_2). These minerals contain sulfur that is loosely held or "labile" which is given off by melting the minerals.

$$2CuFeS_2 = Cu_2S + FeS + S$$

$$FeS_2 = FeS + S$$

Cu_2S and FeS form matte, whereas the labile sulfur reacts with oxygen in the reverb gases to form SO_2. Removal of the labile sulfur during roasting can reduce emissions from the reverb. Also the lower fuel requirement per ton of charge when using calcine smelting reduces the volume of reverb off-gases.

Both types of roasters (multiple hearth and fluidized bed) usually operate around 1200°F. Sulfur dioxide concentration in the wet off-gas is usually 2-10% with multiple hearth roasters because of dilution with air. With fluid bed roasters the wet off-gases can run 12-14% sulfur dioxide. Both types of roasters, therefore, can produce a steady stream of relatively rich off-gases suitable for sulfuric acid manufacture after cooling and dust removal. Both types of roasters involve handling and collecting of large quantities of hot abrasive dust, which can lead to high maintenance costs.

(4) Reverberatory Furnace Smelting

Roasted and unroasted materials are melted after mixing with suitable fluxes in reverberatory furnaces. Liquid converter slag is also charged into the reverberatory furnace to recover its copper content. Heating of the charge is accomplished by burning fuel in the furnace cavity, the heat being transmitted to the charge primarily by radiation from the roof, walls and flame.

Almost all the reverbs in the United States use natural gas as a fuel and only one plant uses powdered coal. Because of the impending domestic shortage of natural gas, most smelters are now installing facilities to burn alternate fuels. The maximum smelting capacity of a reverb is limited by the amount of fuel that can be burned (a function of reverb shape and size) and the quantity of heat required by a unit weight of charge. Reverb throughput can be increased by drying the charge, preheating the charge by roasting and preheating the combustion air.

In the reverberatory furnace, copper and sulfur form the stable copper sulfide (Cu_2S). Excess sulfur unites with iron to form a stable ferrous sulfide, (FeS). The combination of the two sulfides, known as matte, collects in the lower area of the furnace and is removed. Such mattes may contain from 15-50% copper, with 40-45% copper content being most common, and impurities such as sulfur, antimony, arsenic, iron, and precious metals.

The remainder of the molten mass, containing most of the other impurities and known as slag, being of lower specific gravity, floats on top of the matte and is drawn off and discarded. Slags in copper smelting are ideally represented by the composition $2FeO.SiO_2$, but contain alumina from the various charge material and calcium oxide which is added for fluidity. Since reverb slags are discarded, the copper contained in the reverb slag is a major cause of copper loss in pyrometallurgical practice. The concentration of copper in the slag increases with increasing matte grade. This behavior limits the matte grades normally obtained in conventional reverberatory practice to below 50% Cu.

When using a reverb for green charge smelting, 20% to almost 45% of the sulfur in the feed is oxidized and is removed from the furnace with the off-gases. The wet off-gases can contain 1.5-3% sulfur dioxide. When using calcine smelting, sulfur dioxide evolution is lower and about 10-15% of the sulfur in the unroasted feed material is contained in the reverb off-gases. SO_2 concentration in the wet off-gases in this case can vary between 0.5-1%. In neither case is recovery as H_2SO_4 practical.

The hot gases from the reverb are cooled in waste heat boilers, which extract up to 50% of the sensible heat in the gases. A considerable amount of dust is removed in the waste heat boiler and the gases are further cleaned in electrostatic precipitators before venting to the atmosphere.

Reverberatory furnaces can vary in width from about 22 ft to 38 ft and in length from about 100 ft to 132 ft. The roofs of the older reverberatory furnaces are sprung arch silica roofs, while almost all the newer furnaces have suspended roofs of basic refractory. Over the years two types of reverberatory furnaces have evolved, each with its specific charging methods. The first and older is the deep bath reverberatory furnace which contains a large quantity (in excess of 100 tons) of molten slag and matte at all times. In modern deep bath reverberatory furnaces, the molten material is held in a refractory crucible with cooling water jackets along the sides to greatly diminish the danger of a breakout of the liquid material. In deep bath smelting, several methods exist for charging. Wet concentrates can be charged using slinger belts (high speed conveyors) that spread the concentrates on the surface of the molten bath. Dry concentrates or calcines from the roaster can be charged through the roof or via a Wagstaff gun, (an inclined tube). Roof charging (side charging) is rarely practiced in conjunction with deep bath smelting because of dusting problems with fine dry calcine and explosion problems with green charge. Wagstaff guns minimize these problems and are commonly used.

The second type of reverberatory furnace is the dry hearth type in which a pool of molten material exists only at the tapping end. The dry hearth type furnaces are charged with wet or partially dried concentrates (green feed smelting) or with calcines through the roof. In the latter case the dusting problem can be quite severe for fine concentrates.

(5) Converting

Matte produced in the reverberatory furnace is transferred in ladles to the converters using overhead cranes. The converters used in copper smelting are of the cylindrical Pierce-Smith type, the most common size being 13 ft by 30 ft. Air is blown from the side through a series of openings called tuyeres. During the initial blowing period (the slag blow) FeS in the matte is preferentially oxidized to FeO and Fe_3O_4 and sulfur is removed with the off-gases as SO_2. Flux is added to the converter to combine with iron oxide and form a fluid iron silicate slag. When all the iron is oxidized, the slag is skimmed from the furnace leaving behind "white metal" or molten Cu_2S. Fresh matte is charged into the converter at this stage and the slag blowing continued until a sufficient quantity of white metal has accumulated. When this happens the white metal is oxidized with air to blister copper during the "copper blow". The blister copper is removed from the converter and cast or subjected to additional fire refining prior to casting. Converter blowing rates can vary between 12,000 to 30,000 scfm air. Also, the SO_2 content of the off-gases is lower during "slag blow" than during "copper blow".

Cooling of the hot converter gases is necessary in order to prevent thermal damage to the dry gas cleaning equipment. Normally, this is accomplished by adding dilution air that can vary in quantity from 1-4 times the converter off-gas. With dilution air, SO_2 concentrations in the converter off-gases can vary from 1-7%. With close fitting hoods or with Hoboken converters, the off-gases average 5-10% SO_2. However, when dilution air is not used, such cooling devices as waste heat boilers, air/gas heat exchangers, or water sprays are necessary.

The converter gases pass via a balloon flue or individual high velocity flues to dry gas cleaning equipment such as cyclones or electrostatic precipitators. When these gases are to be used for acid manufacture an electrostatic precipitator for dry gas cleaning is not essential since the wet gas cleaning system (wet scrubber, electrostatic demister, etc.) removes all the particulates from the gas stream. Thus, with proper hooding, the converter off-gas is sufficiently high in sulfur dioxide to be suitable for sulfuric acid manufacture, but converting by its very nature is a batch operation and the off-gas flow rates vary widely. In the smaller copper smelters that use two or three converters, the scheduling of converter blows in order to obtain relatively steady flows to the acid plant is a difficult problem.

d. Refining

The blister copper produced by smelting is too impure for most applications and requires refining before use. It may contain silver and gold, and other elements such as arsenic, antimony, bismuth, lead, selenium, tellurium, and iron. Two methods are used for refining copper - fire refining and electrolysis.

The fire-refining process employs oxidation, fluxing and reduction. It is based on the weak affinity of copper for oxygen as compared with that of the impurities. The molten metal is agitated with compressed air, sulfur dioxide is liberated, and some of the impurities form metallic oxides, which combine with added silica to form slag. Sulfur, zinc, tin, and iron are almost entirely eliminated, and many other impurities are partially eliminated by oxidation. Lead, arsenic, and antimony can be removed by fluxing and skimming as a dross. After the impurities have been skimmed off, copper oxide in the melt is reduced to metal by inserting green wood poles below the bath surface (poling). Reducing gases formed by combustion of the pole convert the copper oxide in the bath to copper. In recent years, reducing gases such as natural gas or reformed natural gas have been used. If the original material does not contain sufficient gold or silver to warrant its recovery, or if a special purpose silver-containing copper is desired, the fire-refined copper is cast directly into forms for industrial use. If it is of such a nature as to warrant the recovery of the precious metals, the fire refining is not carried to completion but only far enough to insure homogeneous anodes for subsequent electrolytic refining.

In the electrolytic refining step, anodes and cathodes (thin copper starting sheets) are hung alternately in concrete electrolytic cells containing the electrolyte which is essentially a solution of copper sulfate and sulfuric acid. When current is applied, copper is dissolved from the anode and an equivalent amount of copper plates out of solution on the cathode. Such impurities as gold, silver, platinum-group metals, and the selenides and tellurides fall to the bottom of the tank and form anode slime or mud. Arsenic, antimony, bismuth, and nickel enter the electrolyte. After the plating cycle is finished, the cathodes are removed from the tanks, melted, and cast into commercial refinery shapes. The copper produced has a minimum purity of 99.9%. The anode slime is treated for recovery of precious metals.

APPENDIX B

GLOSSARY

Anode copper - Copper 98-99% pure produced in a smelter cast into a specific shape for electrorefining.

Blister copper - copper produced by a smelter. Chemically the same as anode copper but cast into other shapes.

Cathode copper - copper 99%+ pure produced via electrolytic deposition.

Toll smelting - the smelting of concentrates owned by an independent mine for a charge ("toll charge") and returning the copper.

Custom smelting - the purchase of concentrates produced by an independent mine for smelting.

Matte - mixture of copper and iron sulfide produced during smelting.

Roasting - high temperature partial oxidation of sulfides without melting.

Calcine smelting - the charging of roasted concentrates to a smelting unit.

Green feed smelting - the charging of concentrates directly to a smelting unit without roasting.